GRAFTING OF POLYSTYRENE TO POLY(ETHYLENE-*ALT*-TETRAFLUOROETHYLENE) (ETFE) FILMS BY CONTROLLED RAFT POLYMERIZATION IN THE PRESENCE OF A CROSSLINKING AGENT

POLİ(ETİLEN-*ALT*-TETRAFLOROETİLEN) (ETFE) FİLMLERE KONTROLLÜ RAFT POLİMERİZASYONU İLE ÇAPRAZ BAĞLAYICI BİR AJAN VARLIĞINDA POLİSTİREN AŞILANMASI

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ABSTRACT

GRAFTING OF POLYSTYRENE TO POLY(ETHYLENE-*ALT*-TETRAFLUOROETHYLENE) (ETFE) FILMS BY CONTROLLED RAFT POLYMERIZATION IN THE PRESENCE OF A CROSSLINKING AGENT

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Controlling the molecular weights and distributions of polymers is not possible in syntheses carried out by conventional Free Radical Polymerization (FRP). This hinders the widespread use of FRP techniques in the synthesis of polymers with well-designed molecular structures. On the other hand, Controlled Free Radical Polymerization (CRP) methods have emerged as promising methods in which the polymer weight and distribution can be controlled. Among the CRP methods, Reversible Addition-Fragmentation Chain Transfer (RAFT), which is the only method that can be carried out under radiation, seems quite advantageous since it is suitable for the polymerization of almost all vinyl monomers and can be carried out using a wide range of solvent and temperature alternatives [1]. As the polymers synthesized by Controlled Free Radical Polymerization methods have well-designed molecular structures, they can be used effectively in many different fields such as preparation of sensor materials, polymer-protein conjugates, development of polymeric materials with cylindrical, spherical, hyper-branched architectures, and pH or temperature responding smart polymers, etc. [2].

Polymer Electrolyte Membrane Fuel Cells (PEMFC, also knowns as Proton-Exchange Membrane Fuel Cells) that directly convert the energy of the fuel into electrical energy through a series of electrochemical reactions have an important place among the various fuel cells as they can be used in transportation and small-sized power generation systems due to benefits such as increased power density, immediate response to changes in power demand, and low operating temperatures. Since the first electrically powered automobile was developed using the PEMFC system, many different types and models of vehicles have used these systems, which use hydrogen as the fuel and convert it into electricity. One of the most important factors determining the cost is the membranes that are needed during passage of substances in the electrolyte system. The most common material used as Polymer Electrolyte Membrane PEM is Nafion produced by DuPont. However, due to the high cost of this membrane, it is challenging for electric vehicles to replace existing ones that use fossil fuels. For this reason, many studies aiming to synthesize new membranes to increase the performance of existing systems and reduce costs have gained great momentum, especially over the last few decades.

One of the most widely applied methods to develop low-cost and high-performance alternative PEMs is to provide the functionality required for proton conductivity to fluorinated or partially fluorinated polymer films with the desired properties by conventional radiation-induced grafting (RIG) method. Conventional Free Radical Polymerization technique has been used for the grafting process in the studies carried out so far. However, it is not possible to achieve the desired structural control with this method. The advantages of the CRP methods for the preparation of PEMFC have been demonstrated in some studies. However, these studies are insufficient and the application of controlled polymerization methods in the presence of a crosslinking agent and using the Radiation Induced Grafting Technique for the preparation of PEM is not available in the literature.

In this thesis, by applying radiation-induced and RAFT-mediated graft copolymerization of polystyrene from the cost-efficient ETFE films using a crosslinker (divinyl benzene, DVB) for the first time, a well-defined PEM will be obtained. Compared to PEMs synthesized by conventional methods, it is aimed to synthesize unique PEMs with superior properties, especially in terms of proton conductivity, thanks to the structural control and homogeneity to be achieved by the RAFT mechanism.

Membranes with different degrees of grafting prepared within the scope of the thesis were characterized by ATR-FTIR, SEM-EDX, AFM, TGA, XPS, and DMA techniques. These extensive characterizations were used to confirm the presence of grafted polystyrene (PS) chains in copolymer compositions and the success of sulfonation. In summary, it was seen from the ATR-FTIR results that the syntheses were performed successfully, and when the AFM images were examined, it was observed that the surface roughness increased because of grafting. The results from DMA and TGA provided significant and promising details regarding the mechanical and thermal performance of the membranes. It was determined that the chemical resistance of the membranes synthesized in the presence of DVB increased approximately 4 times compared to those synthesized without DVB. Although there was a decrease in proton conductivity due to the use of DVB, a significant increase in chemical stability emerged as a result of cross-linking reactions. Membranes with 45% and 67% degrees of grafting exhibited higher proton conductivity than many alternatives in the literature, especially commercial Nafion samples.

Key Words: Polymer Electrolyte Membrane (PEM), RAFT polymerization, Membranes synthesized by radiation-induced grafting, poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), graft copolymerization

ÖZET

POLİ(ETİLEN-*ALT*-TETRAFLOROETİLEN) (ETFE) FİLMLERE KONTROLLÜ RAFT POLİMERİZASYONU İLE ÇAPRAZ BAĞLAYICI BİR AJAN VARLIĞINDA POLİSTİREN AŞILANMASI

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Geleneksel Serbest Radikal Polimerizasyonu (SRP) ile yürütülen sentezlerde, polimerlerin molekül ağırlıklarının ve dağılımlarının kontrol edilebilmesi mümkün değildir. Bu durum SRP tekniklerinin, iyi tasarlanmış moleküler yapılara sahip polimerlerin sentezinde yaygın olarak kullanılmasına engel oluşturur. Diğer taraftan, Kontrollü Serbest Radikal Polimerizasyonu yöntemleri olarak bilinen teknikler ile polimer molekül ağırlığı ve dağılımının kontrol edilebilmesi mümkün olmuştur. Bu yöntemler arasında radyasyonla başlatılabilme özelliğine sahip tek teknik olan Tersinir Katılma-Ayrılma Zincir Aktarım Polimerizasyonu (RAFT- Reversible Addition-Fragmentation Chain Transfer), diğer yöntemlere nazaran neredeyse tüm vinil monomerlerin polimerizasyonuna uygun olması ve oldukça geniş çözücü-sıcaklık alternatiflerinde başarıyla uygulanabilmesi nedeniyle oldukça avantajlıdır [1]. Kontrollü Serbest Radikal Polimerzasyonu yöntemleri ile sentezlenen polimerler, iyi tasarlanmış moleküler yapıya sahip olmaları dolayısıyla, sensör malzemelerin hazırlanması, polimer-protein konjugatları, silindirik, küresel, çok dallı ve benzeri özel mimarideki polimerik

malzemelerin geliştirilmesi ya da pH veya sıcaklık gibi farklı dış etmenlere karşı duyarlı akıllı polimer sistemlerin tasarımı gibi farklı alanlarda etkin olarak kullanılmaktadır [2].

Yakıtın enerjisini bir dizi elektrokimyasal reaksiyon aracılığı ile doğrudan elektrik enerjisine dönüştüren yakıt hücreleri arasında, özellikle Polimer Elektrolit Membranı (PEM) içeren yakıt pilleri (PEMFC, Proton Değişim Membranlı Yakıt Hücresi olarak da bilinirler), ulaşım ve küçük boyutlu enerji üretim sistemlerinde kullanım avantajları ile önemli bir yere sahiptir. PEMFC sistemi kullanılarak geliştirilen elektrikle çalışan ilk otomobilden bu yana, pek çok farklı tür ve modelde taşıt, yakıt olarak hidrojeni kullanıp elektriğe dönüştürme temeline dayanan bu sistemleri kullanmıştır. PEMFC sistemlerinde maliyeti belirleyen en önemli faktörlerden biri elektrolit sistemde madde geçişini sağlayan membranlardır. PEM olarak bilinen bu membranlarda kullanılan en yaygın malzeme, DuPont firması tarafından üretilen Nafion'dur. Fakat bu membranın maliyetinin çok yüksek olması elektrikli araçların, fosil yakıtlarını kullanan mevcut araçların yerini almasını zorlaştıran parametrelerden biridir. Bu sebeple mevcut sistemlerin performasının artırılması ve maliyetlerin düşürülmesi için yeni membranların sentezlenmesini amaçlayan çalışmalar özellikle son yıllarda büyük hız kazanmıştır.

Düşük maliyetli ve aynı zamanda yüksek performans gösteren alternatif PEM malzemelerin geliştirilmesinde izlenen en temel yollardan biri, istenilen mekanik ve termal özelliklere sahip, ancak aynı zamanda düşük maliyetli florlu polimer filmlere, radyasyonla başlatılmış aşılama tekniği ile proton iletkenliği için gerekli olan fonksiyonelliğin kazandırılmasıdır. Bu zamana kadar yürütülen çalışmaların pek çoğunda, aşılama işlemi için Geleneksel Serbest Radikal Polimerizasyon (SRP) tekniği kullanılmıştır. Fakat istenilen üst düzey yapısal kontrolün sağlanması bu yöntemle mümkün değildir. PEMFC hazırlanması için Kontrollü Polimerizasyon Yöntemlerinin (KPY) avantajları önceki bazı çalışmada ortaya konmuştur. Ancak bu çalışmalar yetersizdir ve Radyasyonla Başlatılmış Aşılama Tekniği ile bir çapraz bağlayıcı ajan varlığında kontrollü polimerizasyon yöntemlerinin PEM hazırlanması amacıyla uygulaması literatürde mevcut değildir.

Bu tez çalışmasında, uygun maliyetli poli(etilen-*alt*-tetrafloroetilen) (ETFE) filmlere radyasyon başlatıcılı kontrollü RAFT Polimerizasyonu ile çapraz bağlayıcı bir ajan varlığında (DVB) polistiren aşılanarak, elde edilen aşı kopolimer filmin sülfolanması ile PEM elde edilmesi amaçlanmıştır. Geleneksel yöntemlerle sentezlenen PEM'lere kıyasla RAFT mekanizmasıyla sağlanacak yapı kontrolü ve homojenlik sayesinde, başta proton iletkenliği olmak üzere, daha üstün özelliklere sahip özgün PEM'lerin sentezlenmesi hedeflenmiştir.

Tez kapsamında hazırlanan farklı aşılama derecelerine sahip membranlar ATR-FTIR, SEM-EDX, AFM, TGA, XPS ve DMA teknikleri ile karakterize edilmiştir. Bu kapsamlı karakterizasyonlar, kopolimer bileşimlerinde aşılanmış polistiren (PS) zincirlerinin varlığını ve sülfonasyonun başarısını doğrulamak için kullanılmıştır. Özetle, ATR-FTIR sonuçlarından sentezlerin başarıyla gerçekleştirildiği anlaşılmış, AFM görüntüleri incelendiğinde aşılama sonucunda yüzey pürüzlülüğünün arttığı görülmüştür. DMA ve TGA'dan elde edilen sonuçlar, membranların performansı ve mekanik-termal kararlılığı ile ilgili önemli ve umut verici sonuçlar sağlamıştır. DVB varlığında sentezlenen membranların kimyasal direncinin, DVB olmadan sentezlenenlere kıyasla yaklaşık 4 kat arttığı tespit dilmiştir. DVB kullanımına bağlı olarak proton iletkenliğinde azalma olmasına rağmen kimyasal kararlılıkta önemli bir artış olması, çapraz bağlanma reaksiyonlarının olumlu bir sonucu olarak ortaya çıkmıştır. %45 ve %67 aşılama oranına sahip membranlar, literatürdeki pek çok alternatiften ve bilhassa ticari Nafion örneklerinden daha yüksek proton iletkenliği sergilemiştir.

Anahtar sözcükler: Polimer Elektrolit Membran (PEM), RAFT polimerizasyonu, radyasyonla aşılanarak elde edilen membranlar, poli(etilen-*alt*-tetraflororoetilen) (ETFE), aşı kopolimerizasyonu

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Nazlıcan YILDIRIM
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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AFC	Alkaline Fuel Cells
AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflection
ATRP	Atom Transfer Radical Polymerization
BrTFF	2-bromotetrafluoroethyl trifluorovinyl ether
CRP	Controlled Free-Radical Polymerization
CA	Contact Angle
DC	Direct Current
DVB	Divinylbenzene
DDMAT	2- (dodecylthiocarbonothioylthio) -2-methyl propionic acid
DMA	Dynamic Mechanical Analysis
DG	Degree of Grafting
EDX	Energy Dispersive X-Ray Analysis
EPR	Electron Paramagnetic Resonance Spectroscopy
ETFE	Poly(ethylene-*alt*-tetrafluoroethylene)
ETFE-g-PS	Polystyrene-grafted ETFE film
ETFE-g-PSSA	Membranes of the sulfonated version of ETFE-*g*-PS film
EW	Equivalent Weight
FRP	Free-Radical Polymerization
FEP	Fluorinated Ethylene Propylene
FTIR	Fourier Transformation Infrared Spectrophotometer
GPC	Gel Permeation Chromatography
GDL	Gas Diffusion Layer
IEC	Ion Exchange Capacity
MEA	Membrane Electrode Assembly
MCFC	Molten Carbonate Fuel Cells
NMP	N-Methyl-Pyrrolidone
PSSA	Polystyrene Sulfonic Acid
PEMFC	Proton Exchange Membrane Fuel Cells

PEM	Proton Exchange Membrane
PAFC	Phosphoric Acid Fuel Cells
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PI	Polyimide
PEEK	Poly (ether ether ketone)
PES	Poly (ether sulfone)
PBI	Poly (benzimidazole)
PPZ	Poly (phosphazene) hydrocarbon polymers
PVDF	Polyvinylidene fluoride
PFA	Perfluoroalkoxy alkanes
PTFE	Polytetrafluoroethylene
SFRP	Stable Free Radical Polymerization
SEM	Scanning Electron Microscopy
St	Styrene
SOFC	Solid Oxide Fuel Cells
RAFT	Reversible Addition-Fragmentation Chain Transfer Polymerization
RIG	Radiation-induced grafting
TGA	Thermogravimetric Analysis
XPS	X-ray Photoelectron Spectroscopy (XPS)
UNAM	Bilkent University National Nanotechnology Research Center
IDT	Initial Decomposition Temperature
MRDT	Maximum Rate Decomposition Temperature

Symbols

M	Monomer
Mn	Number average molecular weight
Mw	Weight average molecular weight
Tg	Glass Transition Temperature
R_a	Roughness Value

E'	The loss module of the polymer
E''	The storage module
IEC_{teo}	Theoretical Ion-Exchange Capacity
IEC_{exp}	Experimental Ion-Exchange Capacity
M_{St}	Molar mass of styrene (104.15 $gmol^{-1}$)
M_{SSA}	The molar mass of Styrene sulfonic acid (184 $gmol^{-1}$).
M_{NaOH}	Molarity of NaOH
V_{NaOH}	Volume of NaOH
W_{memb}	Membrane mass
W_{ξ}	The weight of the water-swollen membrane
W_d	The dry weight of the vacuum-dried membrane
λ	Hydration number of the membrane
φ_w	Water uptake
W_i	Initial mass of non-grafted ETFE film,
W_f	Final mass of grafted ETFE copolymer film
M_{CPDA}	The molar mass of RAFT agent (DDMAT)
n_{St}^0	The initial number of moles of monomer (Styrene + DVB)
n_{CPDA}^0	Number of moles of RAFT agent (DDMAT)
M_{St}	Molecular weight of the monomer (Styrene)
σ	Proton conductivity value
R (Ω)	The membrane resistance
A	The membrane cross-sectional area
L	The thickness of the membrane

1. INTRODUCTION

Fossil fuels supply about 80% of the world's energy needs. These fuels are known to cause harmful gas emissions to the environment and human health. In addition to this familiar problem, fossil fuels are criticized by both non-governmental organizations and society as they are limited and cause many other environmental issues such as global warming. The tendency to alternative energy sources instead of fossil fuels is increasing day by day.

There are not enough fossil fuel reserves to meet the rapidly increasing energy demand soon. For this reason, research on renewable and sustainable energy systems have been carried out intensively in recent years. Besides being one of the most abundant elements globally, hydrogen can be used in fuel cell systems and thus provide clean energy. While the energy conversion efficiency of fossil fuels is between 15-35%, this conversion can reach 80% in fuel cells. [3]. Fuel cells can be used in multiple devices, especially in heavy tonnage land vehicles, mobile phones, laptops, and even aircraft. Therefore, it is crucial to develop fuel cell technologies for the well-being of human society.

First introduced by Sir William Grove, the fuel cell concept can simply be defined as an energy conversion device. Fuel cells are classified according to the operating temperature of the electrolyte and the type of fuel used. Different fuel cell types are given below:

- Alkaline Fuel Cell (AFC),
- Phosphoric Acid Fuel Cell (PAFC),
- Polymer Electrolyte Membrane Fuel Cell (PEMFC),
- Molten Carbonate Fuel Cell (MCFC),
- Direct Methanol Fuel Cell (DMFC),
- Solid Oxide Fuel Cell (SOFC) [3].

The structure of all these fuel cells consists of a design that uses two electrodes divided by a solid or liquid electrolyte that moves or conducts electrically charged particles between them. A catalyst is often used to speed up reactions at the electrodes.

High efficiency, quiet operation conditions, modular structures, wide range of different fuel types, low emissions, high reliability, easy installation, efficient energy conversion and cogeneration can be counted among the advantages that are effective in choosing fuel cells. However, the high costs and lack of performance/durability are the main obstacles for fuel cells to replace existing energy sources. Nowadays, intensive studies are carried out in many countries to overcome these obstacles and develop new fuel cell membranes.

The membrane named Nafion, which was developed by DuPont company and has very superior properties, is preferred as the Polymer Electrolyte Membranes (PEMs). Since it is a fluorinated membrane, it is a polymer with high chemical, thermal and mechanical stability, and additionally very good proton conductivity. However, despite all these superior features, Nafion has some disadvantages. Its high cost is one of its biggest drawbacks. Additionally, drawbacks such as difficult synthesis of Nafion requiring complex fluoride chemistry, proton carrier capacity loses at high temperatures, and high methanol permeability have revealed the fact that an alternative membrane should be found [4].

Among the studies developed to prepare PEMs as alternatives to Nafion, the most common one is radiation-mediated graft copolymerization. In this method, a polymer film that has high mechanical, thermal and chemical stability such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) is used as the main polymer backbone, and a monomer that provides proton carrier properties is grafted onto this structure using ionizing radiation [5, 6].

Generally, sulfonic acid and carboxylic acid groups are used as functional groups. The reason why the sulfonic acid groups are used most widely is that they have a very high proton carrying capacity due to their high acidity [7]. Grafting monomers like styrene, which is preferred because it is an inexpensive monomer, to the fluorinated polymer films and subsequent attachment of the sulfonic acid group to the structure by sulfonation is the most applied way to obtain a sulfonated fluorinated membrane [5].

ETFE has some advantages over other fluorinated polymers. The high mechanical strength, radiation stability and high degree of grafting at low doses are important reasons for its preference. Due to these advantages, ETFE has been widely used in research on the preparation of PEMs in recent years [8, 9].

It is expected that membranes with superior properties can be prepared if the length and frequency of the grafted polystyrene chains can be controlled. For this reason, reversible addition−fragmentation chain-transfer (RAFT) polymerization method, which is one of the Controlled Radical Polymerization (CRP) techniques, has been preferred in the scope of this thesis instead of conventional free-radical polymerization method applied widely in the literature.

Many properties of membranes can be improved using crosslinkers during polymerization [10]. There are many examples in literature where the radiation mediated grafting is applied under conventional polymerization conditions using crosslinkers [10, 11]. Crosslinking of PEMs using special agents such as divinylbenzene (DVB) is commonly applied for fluoropolymers in the preparation of radiation-induced grafted membranes due to the significant and positive influences on properties such as mechanical strength and thermal/chemical stability despite some negative impacts on water uptake and proton conductivity compared to other methods [12, 13].

In this thesis, PEMs will be obtained for the first time in the literature by grafting of polystyrene to inexpensive ETFE films by radiation-induced controlled RAFT polymerization method in the presence of a crosslinking agent (DVB). Compared to PEMs synthesized by conventional methods, thanks to the structural control and homogeneity achieved by the RAFT mechanism, unique PEMs with superior properties are aimed to be synthesized. Membranes with various degrees of grafting were characterized by ATR-FTIR, SEM-EDX, AFM, TGA, XPS, and DMA techniques. These extensive characterizations were used to confirm the presence of grafted polystyrene (PS) chains in copolymer compositions and the success of sulfonation. One of the most important gains is the membranes with 45% and 67% degrees of grafting (DG) exhibited higher proton conductivity than many alternatives in the literature, especially compared to commercial Nafion samples. It was also determined that the chemical stability of the membranes synthesized in the presence of DVB was approximately 4 times higher than those synthesized without DVB. Although there was a decrease in proton conductivity due to the use of DVB, a significant increase in chemical stability emerged as a result of cross-linking reactions.

2. GENERAL INFORMATION

2.1. Fuel Cells

Fuel cells are energy converters that produce electricity from the chemical energy stored in fuels [14]. A fuel cell is an electrochemical device that combines hydrogen and oxygen as byproducts with water and valuable heat to generate electricity [15]. A fuel cell is one of the essential energy converters and have advantages of high conversion efficiency and high reliability [14].

Fuel cells offer a special combination of benefits that make them an essential technology suitable for many applications. The benefits of Fuel Cells can be summarized as follows:

- Fuel flexible - operation on conventional or renewable fuels
- High quality, reliable power
- Exceptionally low/zero emissions
- Can be used with or instead of batteries and diesel generators
- Cooperative use with solar, wind, and other renewable technologies
- Increased productivity
- Cost savings via high electrical and overall efficiency
- Fuel cells are operating in several market segments today. [15]

2.1.1. History of Fuel Cells from Past to Present

The basis of fuel cells with the principle of generating electricity from gaseous fuel is based on the discovery of Sir William Grove in 1839 [16]. The "gaseous voltaic cell" built by him generated electricity and water upon reaction of hydrogen and oxygen. The fuel cell used porous platinum electrodes and sulfuric acid as the electrolyte. William White Jaques, who substituted phosphoric for sulfuric acid as the electrolyte, propounded the term "Fuel Cell." There have been some other important attempts to build fuel cells for many years [17]. The Swiss scientist Christian F. Shoenbein, unaware of his discovery, came up with the same idea simultaneously [18]. This claim, which is called a gaseous voltaic battery by Grove [19], has not been possible for a long time to be turned into a practically applicable device, despite some experimental studies [20]. In 1937, Francis T. Bacon studied the practical applications of fuel cells and developed the first 6 kW fuel cell in 1950. However, the first applications of fuel cells were carried out by the American Space Program [21].

Subsequently, PEM fuel cells were used to meet the electricity needs of some vital units in the Apollo Space Program. In the mid-1960s, the General Motors company developed a fuel cell-powered pickup truck. Although the American Space Program has continued to use fuel cells as of this date, fuel cells were not used in other areas until the early 1990s. Perry Energy Systems, a Canadian company, succeeded in producing a submarine powered by PEM fuel cells in 1989. Ballard Power Systems developed a bus-powered PEM fuel cell in 1993. [22]. Perry Energy Systems firm also developed the first car powered by PEM fuel cell in 1993.

Near the end of the last century, almost all automobile manufacturers operating in the United States produced fuel cell-powered vehicles within a program supported by the United States Department of Energy. Thus, a new industry branch was born, and the revenues of PEM fuel cell manufacturers such as Ballard and PlugPower increased thanks to this new technology rapidly. In recent years, there has been a significant increase in the number of patents related to fuel cells worldwide, especially in America and Japan. Besides, the number of scientific and engineering research in this field is increasing rapidly [23].

2.1.2. Types of Fuel Cells

It is possible to classify fuel cells depending on type of the electrolyte, type of the ion exchanged by the electrolyte, the operating temperature and pressure, the type of reagents, and the direct and indirect use of primary fuels in the fuel cell system. The most suitable classification is based on the type of electrolyte used [3]. Also, the operating temperatures and all other factors depend on the type of electrolyte. Because of this, the electrolyte is playing an important role. Thus, based on this classification, fuel cells include the following different types [24]:

a. *Alkaline Fuel Cells (AFC)*

KOH is the electrolyte in alkaline fuel cells. Generally, these fuel cells are operated with concentrated (85 wt. %) KOH at temperatures as high as 250 °C. A wide variety of catalysts is used in these fuel cells.

b. *Proton Exchange Membrane Fuel Cells (PEMFC)*

Ion exchange membrane electrolyte can be used in fuel cells. These membranes are suitable conductors of protons. Pure water is the byproduct in this type of fuel cells. Polymer membranes' operation temperatures are below 120 °C. If byproducts are considered, these are the most favored fuel cells. However, pressure equilibrium across the membrane and humidity in the cell require precision consideration.

c. *Phosphoric Acid Fuel Cells (PAFC)*

Concentrated phosphoric acid is the electrolyte in this type of fuel cell. The fuel cell is operating temperatures at around 150-200 °C. The matrix used to retain the electrolyte is silicon carbide and platinum is the catalyst used in both the anode and cathode. PAFC minimizes water vapor pressure thanks to the use of concentrated acid (100%). Therefore, water management is not difficult.

d. *Molten Carbonate Fuel Cells (MCFC)*

Combination of alkaline carbonates of Na and K is the electrolyte in molten carbonate fuel cells. The fuel cell operates at 600-700 °C. The Ni anode and nickel oxide cathode can operate with no catalysts at high temperatures compare with other cells.

e. *Solid Oxide Fuel Cells (SOFC)*

A solid non-porous metal oxide (usually Y_2O_3 stabilized ZrO_2) is used as the electrolyte. The fuel cells operate between 650 °C and 1000 °C, where ionic conductivity occurs with oxygen ions.

Summary of the types of the fuel cells is shown in Table 2.1 below [20]:

Table 2.1 Types of the Fuel Cells

Full Cell Type	Electrolyte	Charge Carrier	Fuel	Operation Temp.
AFC	KOH	OH^-	Pure H_2	$60°–120°C$
PEMFC	Solid Polymer	H^+	Pure H_2, tolerates CO_2	$50°–100°C$
PAFC	Phosphoric Acid	H^+	Pure H_2, tolerates CO_2	$\sim 220°C$
MCFC	Lithium and potassium carbonate	CO_3^{2-}	H_2, CO, CH_4, tolerates CO_2	$\sim 650°C$
SOFC	Yttria, Zirconia	O^{2-}	H_2, CO, CH_4, tolerates CO_2	$\sim 1000°C$

2.1.3. Polymer Electrolyte Membrane Fuel Cells (PEMFC)

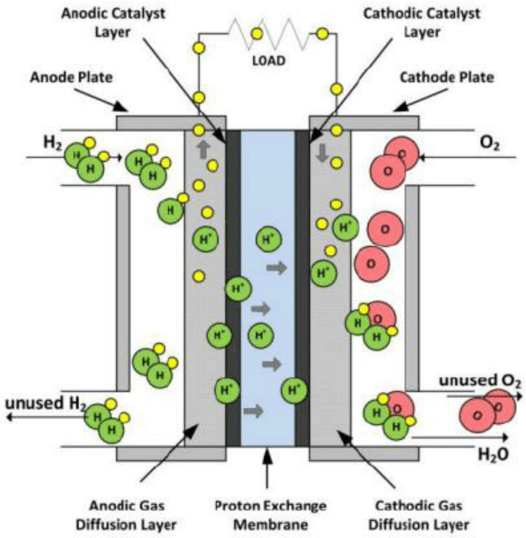
Polymer Electrolyte Membrane (PEM) Fuel Cells (PEMFC) are supposed to will have a critical place in the energy requirement that will increase in the coming years [25]. PEMFC is considered an essential device in so-called “hydrogen-based energy systems” which is a hopeful alternative to the current fossil fuel-based energy system [26]. The transportation sector has a share of approximately 20% of total energy consumption in our country and the world [27]. Fuel cells, mainly containing Polymer Electrolyte Membranes (PEMs), are essential for the transportation sector, as they can use in the automotive industry and small-sized portable systems. For this reason, aims to develop PEMs that can be used in PEMFC systems are continuing very intensively.

PEM fuel cells have the highest power density among existing systems alternatives. It is the fastest in terms of start-up characteristics, and at the same time, it has a compact structure. In addition, it is suitable for the use of atmospheric air since it is not very sensitive to CO_2. For these reasons, it is suitable for use in portable power applications and automotive industries [28].

The central unit of PEM fuel cells is the membrane-electrode junction (Membrane Electrode Assembly, MEA). MEA has a “sandwich” structure consisting of two conductive plates (Figure *2.1*). The PEMFC components are Anode Plate, Anode Gas Diffusion Layer, Anode Catalyst Layer, Cathode Catalyst Layer, Cathode Gas Diffusion Layer, Proton Exchange Membrane and Cathode Plate [26].

The gas diffusion layer (GDL) and the catalyst layer are placed on both sides of the PEM with GDL and then the catalyst on the outside. In addition to providing material passage in the electrolyte system, the membrane acts as a barrier separating the anode and cathode components from each other. Conductor plates involve integrated flow fields, thus ensuring optimal distribution of the gas within the MEA. Electrical current is collected from the battery by current collectors.

Hydrogen and oxygen gases are sent to the anode and cathode, respectively. Hydrogen gas is oxidized to its protons and free electrons at the anode. Electrons flowing through the external circuit producing electrical energy through the external charge reach the cathode to participate in the oxygen reduction producing oxide anions. Protons diffuse from the membrane towards the cathode side and combine with oxide anions to form water molecules.



Anode:
$H_2 \rightarrow 2H^+ + 2e^-$

Cathode:
$\frac{1}{2} O_2 + 2\,H^+ + 2e^- \rightarrow H_2O$

Figure 2.1 Schematic representation of PEMFC [12]

In the PEMFC, hydrogen (H_2) reacts with oxygen (O_2), producing electrical energy, heat, and water, and catalysts like platinum are used to adsorb hydrogen. In terms of the byproducts, PEMFC is the most preferred type of fuel cells. However, pressure equilibrium across the membrane and humidity in the cell require precision consideration [24].

Since the operating temperatures of PEM fuel cells are not too high (60-80 ºC), a noble metal catalyst must be used to accelerate the reactions at the anode and cathode. Therefore, noble metal, and noble metal alloys have been developed as catalysts for hydrogen oxidation and oxygen reduction reactions. Catalysts with a particle diameter of a few nm are embedded in carbon particles with a particle diameter of ~ 50 nm to increase the surface area of the reaction [10, 19]. The gas diffusion layer works as a diffusion medium that allows the reactants to reach the active surface homogeneously. The gas diffusion layer is characterized by its pore structure (~ 50%). The gas diffusion layer ensures that the spent and generated electrons are transmitted from the catalyst to the flow field plates. Also, it plays an essential role in transporting the water generated during the fuel cell operation and the cathode. It, therefore, has a direct effect on performance losses.

For this reason, the hydrophobicity of the diffusion medium must be increased in fuel cells. MEA's electrodes are covered with flow field plates to ensure contact at both electrodes. Stainless steel or non-corrosive graphite is most widely used for flow field plates. Their primary function is to provide the dispersion of gases, transmit electrical current and heat, facilitate water and thermal tolerance within the battery. Channels are machined on graphite plates, and thus flow fields are created to fulfill all of these. Many flow field geometries and designs are from simple to highly complex developed by manufacturers and research groups [30]. Proton transfer from anode to cathode is a very complex process. The main challenge is to create a path for protons to flow. There are known two basic proton transport mechanisms. The first is the vehicular mechanism; the second is the proton hopping or Grotthus mechanism [31]. In the vehicular mechanism, the proton is transported by a vehicle, such as an H_3O^+. In the Grotthus mechanism, the proton occurs by molecular orientations and proton displacement. Protons are transported over water molecules bonded by hydrogen bonds.

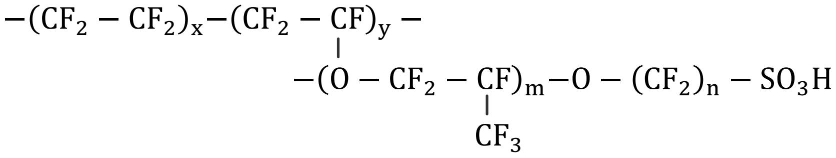
The most critical parameters that determine the cost in fuel cells are the noble metal catalyst and the PEM membrane, which enables material passage in the electrolyte system. PEM is indispensable for MEA. [32]. The vital requirements for polymer membrane electrolyte materials of PEMFC include:

- Proton conductivity
- Thermal and chemical stability
- Mechanical properties such as strength, flexibility, and processability
- Low gas permeability
- Low water drags
- Fast kinetics for electrode reactions
- Low cost and ready availability. [33]

2.1.4. Membranes used in Polymer Electrolyte Membrane (PEM) Fuel Cells

Proton carrier membranes used commercially in today's technology are Nafion-type membranes, the first perfluoro sulfonic acid membrane improved in the 1960s [34]. Many companies commercially produce Nafion and other perfluoro sulfonic acids (PFSA) membranes with highly superior properties. Some typical commercial PFSA membranes consisting of carbon-fluorine backbone chains with perfluoro side chains containing sulfonic acid groups are listed in Table 2.2 [33].

Table 2.2 Commercial PFSA Membranes



$$\begin{array}{l}-(\mathrm{CF_2}-\mathrm{CF_2})_x-(\mathrm{CF_2}-\underset{|}{\mathrm{CF}})_y- \\ \qquad\qquad\qquad -(\mathrm{O}-\mathrm{CF_2}-\underset{\mathrm{CF_3}}{\underset{|}{\mathrm{CF}}})_m-\mathrm{O}-(\mathrm{CF_2})_n-\mathrm{SO_3H}\end{array}$$

Trade Name and Type	Structure Parameter
DuPont Nafion 120 Nafion 117 Nafion 115 Nafion 112	m=1; x=5-13.5; n=2; y=1
Asashi Glass Flemion-T Flemion-S Flemion-R	m=0, 1; n=1-5
Asashi Chemicals Aciplex-S	m=0; n=2-5; x=1.5-14
Dow Chemicals Dow	m=0; n=2; x=3.6-10

Nafion ionomers are obtained by copolymerizing the perfluoro vinyl ether comonomer (perfluoro-3,6-dioxane-4-methyl-7-octene-sulfonyl fluoride) with tetrafluoroethylene (TFE). Nafion, which is processed and transformed into the desired form after synthesis, is firstly hydrolyzed with NaOH or KOH, then protonated with HNO_3 to attain $–SO_3H$ groups [35].

The unrivaled features of Nafion membranes are accepted to be closely related to such phase-separated structures. Not only it was the hydrated hydrophilic domains give high proton conductivity, but moreover their hydrophobic part provides moderately great mechanical stability. Nafion is reasonable for low-temperature proton exchange membrane fuel cells because of these properties. However, there are a couple of impediments in utilizing them for PEMFC applications despite the self-evident focal points of the Nafion membranes. The main drawback of Nafion is its high cost [36]. The overall cost of PEMFC is remarkably raised to this respect.

The other main disadvantage of Nafion is its limited operating temperature. In order to provide suitable proton conductivity, Nafion membranes need to be humidified. For this reason, the membrane must not be dehydrated. However, when the temperature rises above 100 °C, it causes the membrane to dry and the proton conductivity to decrease. Thus, Nafion is not appropriate for fuel cell applications where the temperature exceeds the boiling point of water [33].

The development of sulfonated polymer membranes as alternatives to PFSA is an important development in this field. Numerous polymer materials are prepared, functionalized, and developed as membrane electrolytes for PEMFC [33]. For these, two ways are generally followed. The first is to replace Nafion membranes and in this way find solutions to existing problems. The second way is to improve new membranes based on fluorine-free ionomers or anhydrous proton conductors [37].

Polymer electrolyte membranes divided into three main groups are perfluorinated ionomers, non-fluorinated hydrocarbons, and acid-base complexes [38] are shown in Figure *2.2* [39].

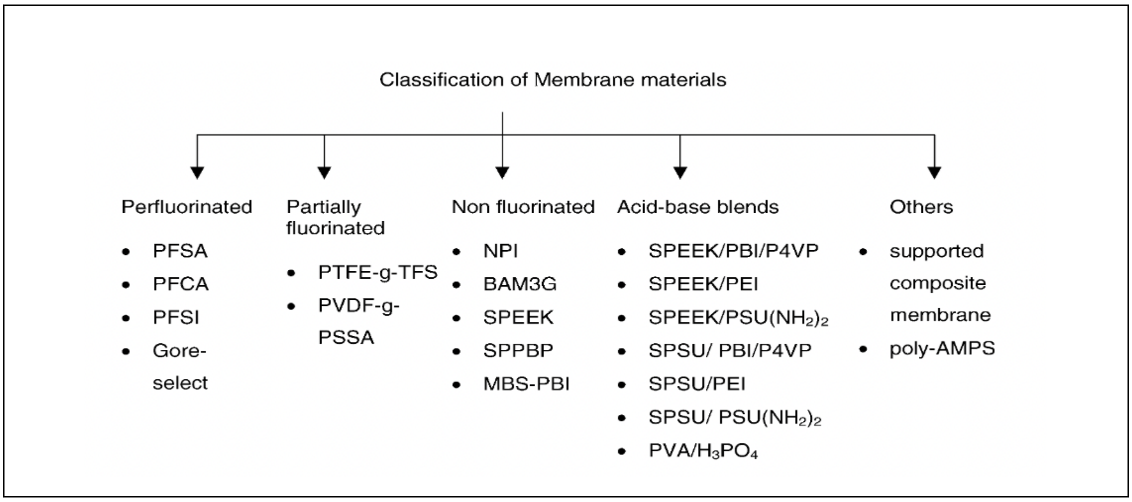


Figure 2.2 Classification of membrane materials

Several approaches have been proposed to develop cheaper alternatives from commercial perfluoro membranes. Non fluorinated hydrocarbon polymers have been studied to create alternative PEMs. The biggest advantage of these membranes is that they are very cheap compared to perfluoro polymers. The difficulty encountered in preparing these membranes is that while the proton conductivity performance is increased, the thermal, mechanical, and chemical stability properties of the main polymer structure cannot be preserved. The degree of sulfation is the main parameter. The increase in ion exchange capacity (IEC) causes the membrane's swelling property to increase, affecting its mechanical properties [40]. Therefore, the membranes mentioned above are not considered as alternative materials to replace Nafion.

The modification of perfluoro, hydrocarbon, or partially fluorinated polymers, which are readily available commercially and already in film form, is another alternative for PEM production. [31, 32]. In general, there are five methods for the modification of PEMs are as follows:

1. Grafting polymerization method by using γ-ray irradiation,
2. Grafting polymerization method by using plasma,
3. The crosslinking method,
4. Sol-gel method,
5. Direct polymerization of suitable monomers

Nowadays, the new membranes including hydrocarbon polymer matrixes, inorganic-organic hybrid membranes, acid-base complexes and grafted ones by irradiation take the place of the Nafion membranes. One of the most interesting and convenient methods for the preparation of proton exchange membranes for fuel cell and other electrochemical applications can be considered as the radiation grafting method [28, 33, 34].

The improving of low-priced and useful PEMs using high energy radiation is an essential steppingstone towards the market introduction of this technology [38]. Furthermore, it has a special place and importance in the literature. Therefore, this effective method used as an alternative way for PEM development is examined in more detail below:

2.1.5. Membranes Obtained by Radiation-induced Grafting

Radiation-induced graft copolymerization, which is one of the convenient methods for the preparation of ion exchange membranes, is preferred because rapid formation of active sites on a suitable polymer matrix can be attained [43]. This polymerization has many advantages such as no need for chemical initiators or catalysts, easy control of grafting degree and ion exchange capacity of membranes. The grafting can be initiated by high-energy irradiation such as γ-rays, electron-beam, etc. The base films, which have a hydrophobic function that prevents the membranes from swelling in water and provide both dimensional stability and mechanical strength, have an important place for polymer electrolyte membranes [44]. In addition, radiation grafted membranes are much more affordable than Nafion membranes [45].

In general, the active centers, i.e., free radicals, formed among the polymer backbone under irradiation behave like macroradicals in radiation-induced graft copolymerization. These radicals initiate graft copolymerization and allow the monomer to be grafted onto the polymer. Thus, a graft-copolymer structure is obtained in which the main backbone consists of the base polymer irradiated and the branches are composed of the grafted chains. By this method, monomers that are difficult to polymerize can form macromolecules at room temperature without the use of initiators or catalysts, and without the need for high temperatures. Another advantage is that graft copolymerization can be carried out regardless of the shape and physical form of the polymer. This is an important advantage in membrane formation. Thus, the step of converting the graft-copolymer film obtained into a thin film is not required later [46]. Radiation grafting can be applied by using in three ways:

a. **Simultaneous radiation-induced grafting:** Both the polymer and the monomer are exposed to radiation in this method. In situ, free radical sites are generated, and the polymerization of the monomer is initiated. The disadvantage of this method is that the monomer is continuously exposed to radiation during the grafting reaction. Also, hereby extensive homo polymerization proceeds parallel to the grafting reaction. This situation causes monomer wastage and a low level of grafting efficiency in the system.

b. **Pre-irradiation grafting method:** This method involves activation of the polymer by exposure to radiation under air, which results in the creation of radicals along the macromolecular backbone. Afterward, these radicals interact with the oxygen and form stable peroxides. The graft polymerization is initiated by the decomposition of these peroxides at high temperatures. The limitation of this process is that significantly high irradiation doses are needed to achieve enough hydroperoxides to accomplish intended graft levels. This situation leads to drastic changes in the physical structure of the polymer and oxidative degradation, even before any grafting is initiated. Afterward this is unfortunately reflected in the membrane characteristics.

c. **Pre-irradiation grafting (trapped radicals' method):** Irradiation of the polymer under an inert atmosphere or under a vacuum is the basis of this method. In this way, radicals are formed that are trapped in the polymer matrix. These radicals then initiate grafting of a monomer [47].

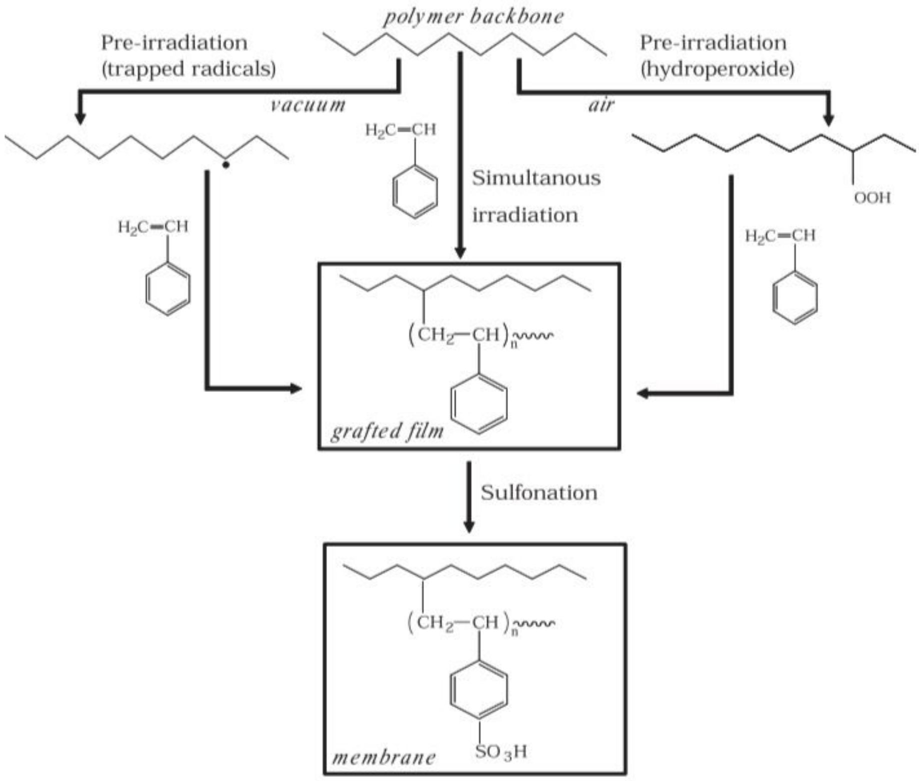


Figure 2.3 Preparation pathways for radiation grafted films and membranes [7]

For radiation-induced graft copolymerization, the main polymer backbone (base polymer) choice is significant. A variety of polymer films such as perfluorinated, partially perfluorinated, and pure hydrocarbon materials are used as the base polymer for the preparation of radiation grafted fuel cell membranes [7]. The base polymer films commonly used are given in Table 2.3 [5].

Polymer film structures can be porous or non-porous (dense). Even though graft copolymerization on porous films is practiced modifying the pores and surfaces of porous films by imparting chemical characters, the greater part of the radiation grafted membranes start with non-porous polymer films [41, 42]. Depending on the chemical structure, crystallinity, melting point, molecular weight of these polymeric materials, better or worse membrane properties can be obtained. The base polymers used for the preparation of PEMs are perfluorinated and partially fluorinated polymers because of their superior properties.

Table 2.3 Common base polymer films used for the preparation of radiation grafted fuel cell membranes

POLYMERS	ABBREVIATION
Perfluorinated Polymers	
Polytetrafluroetylene	PTFE
Poly(tetrafluroetylene-*co*-hexafluoropropylene)	FEP
Poly(tetrafluroetylene-*co*-perfluoropropyl vinyl ether)	PFA
Partially fluorinated Polymers	
Polyvinylidene fluoride	PVDF
Poly(vinylidene fluoride-*co*-hexafluoropropylene)	PVDF-*co*-HFP
Poly(ethylene-*alt*-tetrafluoroethylene)	ETFE
Polyvinyl fluoride	PVF
Hydrocarbon Polymers	
Polyethylene	PE
Polypropylene	PP
Polyvinyl chloride	PVC

Since perfluorinated polymers are more sensitive to radiation and their mechanical properties have significantly decreased as a result of irradiation, partially fluorinated polymers have been used more frequently in recent years. In addition, since partially fluorinated polymers contain hydrocarbon groups, the rate of radical formation by irradiation is higher than perfluorinated polymers [47].

The summary process for the preparation of the new polymer electrolyte membrane is as follows: Pre-irradiation stage, the base films are activated by pre-irradiation in an inert gas at room temperature. It was then grafted with monomers in the substitution stage. In the final step, the grafted films are sulfonated. This is because of introducing sulfonic acid groups into the membranes. The process is completed by hydrolysis in distilled water

[38]. The type of membrane depends on the content of functional groups to be added to the polymer films by grafting. The grafting monomers divided into two categories. One of them is functional or reactive monomers such as acrylic acid, methacrylic acid. The other category is non-functional monomers such as styrene, Nvinylpyridine, and vinyl benzyl chloride [48], [49]. The most common way is to inoculate styrene, a cost-effective monomer, into a fluorinated polymer film, and the sulfonic acid group is subsequently attached to the structure thanks to the easy sulfation of the benzene ring [5].

2.1.6. Controlled Polymerization Methods to be Included in Conventional PEM Preparation Techniques

As mentioned above, one of the most promising alternative techniques for the improvement of new PEM materials is the modification of inexpensive polymer films with desired properties by radiation-induced grafting method. About preparing PEM with this method; monomer type and monomer concentration-effect [19, 43, 44] solvent effect [52], radiation dose rate, and the effect of absorbed dose [43, 44]. The effect of the method applied during radiation grafting [46] the effect of the selected film, and the main polymer crosslinking effect [33, 47] was investigated before.

However, in all these studies, the conventional Free Radical Polymerization (FRP) technique was used while preparing the graft copolymer to add a new polymer with functional properties on the main polymer film. Therefore, the lengths (molecular weights) and molecular weight distributions of the new type of polymer grafted could not be controlled. The fact that the polymer chains grafted on the membrane, which can be qualified as the "heart" of a fuel cell, do not show the same properties at every point of the membrane will significantly affect the features of the membrane. For instance, as mentioned above, the Nafion membrane is named using the ratio of the comonomer carrying the sulfonic acid group to the other monomer, and this ratio is essential for its membrane properties [35]. The ratio of side chains carrying functional groups (e.g., sulfonic acid) to the main chain and the frequency of side chains is a significant parameter that determines the membrane properties. Therefore, grafting of a polymeric film substrate using the conventional free radical polymerization (FRP) method does not allow adjustment of the ratio of functional groups to the main chain. In addition, comparable graft chain lengths (molecular weights) cannot be obtained at all points within the structure.

The main motivation for this thesis work carried out is the point mentioned above. Within the scope of this thesis, it is aimed to include RAFT polymerization, which is one of the most efficient Controlled/Living Radical Polymerization (CRP) methods, in the presence of a crosslinker, instead of the conventional "radiation grafting membrane obtaining" method for the first time in the literature. Previously, in a PhD thesis carried out in our group by Gökçe Çelik [55], polystyrene was grafted from ETFE film by RAFT polymerization, and well-defined PEM structures were obtained by sulfation. However, these structures could not perform mechanically at the desired level as a cross-liner was not applied during the synthesis. For this reason, in this thesis, it is aimed to prepare PEMs by RAFT polymerization using a crosslinker (DVB) since it is known from the literature that PEMs prepared using cross-linkers exhibit higher performance in terms of mechanical and thermal properties.

Thanks to the RAFT polymerization, it is known that not only the polymer formed in solution but also the lengths, more precisely the molecular weights, can be controlled in the polymers grafted onto the surface [50, 51]. Thus, the lengths of the side branches grafted onto the main polymer backbone can be controlled. In addition, it has been reported that grafting performed using the RAFT technique causes a more homogeneous grafting fashion than conventional FRP [50, 51]. All of these are predicted to lead to higher reproducible results and higher proton conductivity values.

The following section provides some information about Controlled/Living Radical Polymerization (CRP), in particular RAFT polymerization, which form the basis of the polymerization procedure applied in this thesis.

2.2. Controlled Free-Radical Polymerization (CRP) Techniques

The conventional free-radical polymerization (FRP) process has many advantages such as tolerance to oxygen, preparing high molecular weight polymers of many vinyl monomers in smooth conditions, adaptability over a large temperature range, etc. [59]. On the other hand, polydispersity, architecture of the polymer and its composition cannot be controlled using this method. However, Controlled/Living Radical Polymerization (CRP) techniques help to eliminate the mentioned disadvantages and hence provide promising alternative synthesis pathways for the preparation of well-defined polymers with controlled molecular weight distributions and predetermined molecular weights [59].

CRP techniques are used effectively to prepare many well-defined structures with specifically controlled structural parameters and can be used to produce materials with new special properties [60]. Synthesis of homo- or co- polymers, such as block, stars, combs, and gradient copolymers has always been challenging in polymer science [61]. All these different polymeric structures have been successfully synthesized using CRP methods [62]. Atom transfer Radical Polymerization (ATRP), Nitroxide Mediated Polymerization (NMP), and Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization are the most recent and widely used controlled/living radical polymerization techniques. They all provide good control over the molecular weight and architecture of the polymers and each of them is effective in the polymerization of a wide range of monomers [63]. Some brief details of ATRP, NMP and RAFT are discussed below:

2.2.1. Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is a polymerization technique using a metal (Mt)/ligand catalyst, developed by Sawamoto et al., Jin-Shan Wang and Krzysztof Matyjaszewski in 1999. [58–60]. Using this method, polymers with quite narrow molecular weight distributions can be synthesized. One of the disadvantages of ATRP is the use of low oxidation state metal salts that have the risk of initiating early oxidation [67].

Transition metals are used as catalysts and alkyl halides are used as initiators in ATRP [68]. Thanks to the special metal catalyst compounds used, different monomers can be added to the growing polymer chain, and new copolymers can be obtained [69]. Catalysts are important in ATRP because they provide atom transfer. Cu and Fe are the most widely used metals used in this method [58–60]. In addition, the solvent has also a significant role in this technique because there can be side reactions involving the catalyst system in a polar medium [67]. In the RAFT mechanism, uniform polymer chains are obtained thanks to the re-initiation step, while in the ATRP mechanism this is achieved by the atom transfer that takes place in the propagation step. This living polymerization technique can be easily stopped and restarted by controlling reaction parameters [70]. The main problem in ATRP is the removal of the catalysts used. The metal catalyst-ligand complex is undesirable in the product because transition metals cause the aging of the polymer and have coloring effects and toxicity. Removal of the catalyst is generally a difficult and expensive process [71].

2.2.2. Nitroxide-Mediated Polymerization NMP

Nitroxide-Mediated Polymerization (NMP) or nitroxide stable free-radical polymerization (SFRP) is a unique technique due to metal-free procedure when it is compared to ATRP. In the NMP mechanism, the initiator decomposes by means of heat and light to form free radicals, and the resulting radicals react with monomers to polymerize them [72]. In a polymerization mechanism carried out by NMP, a stable nitroxide radical, most widely initiated by a molecule named as TEMPO, is used in addition to the initiator. The nitroxide containing compound, such as TEMPO, is the compound that controls the propagation step of the polymerization. The reason why this polymerization method is called nitroxide-mediated polymerization is the nitroxide radical controlling the growth of the polymer chains. In NMP technique, polymers are obtained without a significant purification [73]. However, there are some disadvantages of NMP technique such as long reaction times, availability to a limited number of monomer types and the need for high temperature (125- 145°C) for polymerization [74].

2.2.3. Reversible Addition-Fragmentation Chain Transfer (RAFT)

As one of the most widely used controlled/living radical polymerization techniques, RAFT polymerization was first proposed by the Rizzardo et al. [75]. In the RAFT polymerization, full control is provided by the mechanism that occurs due to the balance in the ratio of dormant and living chains, resulting in living/controlled behavior of polymerization, where RAFT agents are used as reversible chain transfer agents [70, 71] The RAFT polymerization, which is used to obtain narrow molecular weight polymers and block copolymers with pre-determined molecular weights, is a highly efficient and convenient method [78]. The RAFT polymerization is a also suitable method to provide surface functionality and can be used to synthesize a wide range of polymer architectures such as linear, block, star, and hyperbranched [2], [73–75]. Thanks to the RAFT technique, polymers with predictable molecular weights, continuous chain growths, and low dispersities can be synthesized [75].

2.2.3.1. Mechanism of the RAFT Polymerization

The mechanism of RAFT polymerization includes special chain transfer agents, called as RAFT agents, and a series of addition-fragmentation reactions as shown in Figure *2.4* [75]. Free radicals are produced by the first homolytic cleavage of the initiator. The free radicals generated react with the monomer and lead to the formation of the propagating chains (I-II). Thermal initiators such as 2,2'-azobicisobutinonitrile (AIBN) [82] are generally usually used as initiators in the RAFT mechanism. Here, it should be noted that RAFT mechanism can also be carried out using other initiation methods such as ionizing radiation, as the initiation step is quite the same to that of the conventional free-radical polymerization method. Therefore, it is also a method compatible with different initiation mechanisms, such as UV or (gamma) γ-radiation [56].

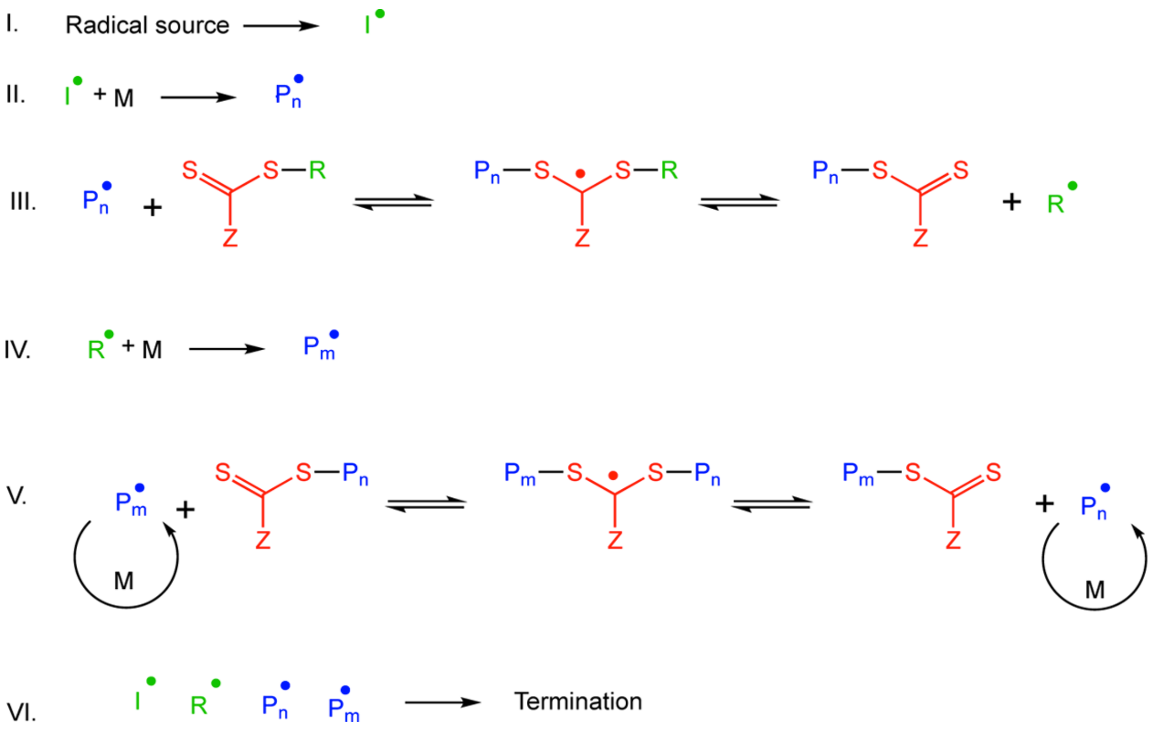


Figure 2.4 Mechanism of Reversible Addition-Fragmentation Chain Transfer (RAFT) polymerization [75]

The addition of a propagating radical (Pn•) to the RAFT agent followed by fragmentation of the intermediate radical gives rise to a polymeric RAFT agent and a new radical (R•) (III). At this stage, if there is a high chain transfer rate constant, this species can also react with a free radical raft agent. This can be prevented by choosing the right RAFT agent.

In the step IV, the RAFT agent obtained radical R• reinitiates polymerization by reaction with monomer to form a new propagating radical (Pm•). Step V where equilibrium is concerned in, active propagating groups and dormant polymeric RAFT agent derived compounds react. The tendency of the macro transition radical in both directions provides an equal probability for all the chains to grow. It is this property of the RAFT technique that causes narrow polydispersity polymers to be produced. Some important factors need to be taken into account for the RAFT process to work properly. The significant considerations are an appropriate rate of initiation and selection of the RAFT agent. In addition, harmony/compatibility is desired between the monomer and RAFT agent [75].

2.2.3.2. RAFT Agent Selection

The success of the reversible chain transfer balance in RAFT polymerization depends on the appropriate RAFT chain transfer agent [79]. Numerous types of RAFT agents are synthesized by considering the functionalities of R and Z groups. A general RAFT agent chemical structure is shown in Figure *2.5* [78].

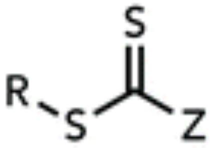


Figure 2.5 Chemical structure of chain transfer agent (CTA) molecules used in RAFT polymerization

CTAs react with radicals or monomers. Therefore, controlled RAFT polymerization is determined by the change in the activation and deactivation mechanisms of CTAs [83]. Using different Z and R groups in CTA structure, a vast range of monomers can be polymerized using the RAFT technique. For the success of the reversible reinitiating reactions, the structure of the R group should be compatible with the related monomer [78, 79]. The Z group also have a strong effect on the success of the RAFT mechanism.

It should give an intermediate product that is less stable than the monomer present in the medium. For this reason, it is critical to make the right selection of monomer and RAFT agent to be used [86].

2.2.3.3. Advantages of RAFT Polymerization Techniques

The significant advantage of the RAFT polymerization is that polymers with low polydispersity and controllable chain length and morphology can be synthesized with more effortless synthesis steps compared to other CRP techniques [82]. Considering the monomer functionality and solvent tolerance, the RAFT method has been the preferred method compared to other CRP methods since it can be used in the polymerization of the wide range of monomers [87].

RAFT polymerization is suitable for bulk, solution, suspension, emulsion, and dispersion polymerizations. In addition, this polymerization can be applied on different substrates, which enables surface modifications and in situ generations of polymer conjugates [88]. The molecular weight of the polymer to be obtained can be controlled by the molar rations of the monomer and RAFT agent used in polymerization [89]. Thus, a polymer structure with low dispersity and pre-determined chain length can be obtained by RAFT polymerization [90]. At the same time, polymers with different architectures such as stars, blocks, brushes can be synthesized by RAFT polymerization [91].

RAFT polymerization is used in less complex and effortless reaction conditions such as low temperature and atmospheric pressure [92]. In addition to these advantages of RAFT polymerization, it is significant for its versatility that it can also be applied in UV-induced [93] or gamma-induced initiation [92] systems, unlike NMP and ATRP [50, 88].

2.3. Controlled Free-Radical Polymerization (CRP) Techniques for the Preparation of PEMs

When the studies in the literature performed using CRP techniques for PEM preparation are examined, it is seen that these techniques are included in the synthesis steps in limited number of publications. First, in 2004, by Holmberg et al., polystyrene was grafted onto PVDF film using the NMP method of CRP techniques, and a well-defined PEM was prepared [95]. In the study conducted by Zhai et al. in 2009, polystyrene was grafted onto

ETFE copolymer film using the ATRP method, another CRP technique, and a fuel cell membrane was prepared [96]. In this study, –Br groups, which act as initiators for ATRP, were included in ETFE structure by radiation grafting of 2-bromotetrafluoroethyl trifluorovinyl ether (BrTFF). However, this grafting step was carried out by conventional free radical polymerization without any control. Following this first uncontrolled grafting step, polystyrene grafting was carried out via ATRP over -Br groups. In this study, where the entire grafting process could not be carried out in a controlled manner, despite this basic disadvantage, relatively high conductivity values (200 mS cm^{-1} at approximately 50% degree of grafting) were obtained. When all the studies in the literature on the preparation of PEM were examined, in the study of Kim and Cho, one of a few studies in which the RAFT technique was applied, PEM was prepared using a completely different method from this thesis subject. Still, the molecular weights of the synthesized polymers or the extent of the targeted control were not questioned [97]. The molecular weights of the grafted chains to which the intended control was aimed were not mentioned in all these studies. As mentioned earlier, CRP techniques in the presence of a cross-liker such as DVB were not used in any previous studies using the *radiation-induced grafting method* which is one of the most widely used methods for developing new PEM materials.

In 2016, we suggested that irradiation of polymer films combined with RAFT-mediated graft polymerization techniques can produce proton exchange membranes with enhanced properties for fuel cell applications [98]. However, as mentioned above, the membranes prepared were not mechanically stable enough as a cross-linker was not applied during the preparation protocol. Many studies in the literature show that CRP techniques exhibit superior properties to free radical polymerization in different applications such as molecular imprinting, toxic metal ion sensor membranes, smart polymeric materials, etc. Therefore, membranes to be synthesized within the scope of the thesis are expected to have promising properties to their existing counterparts. The results verify this prediction and form the basis of the related thesis as mentioned in the following sections.

2.4. Crosslinked Polymer Synthesis using CRP Techniques

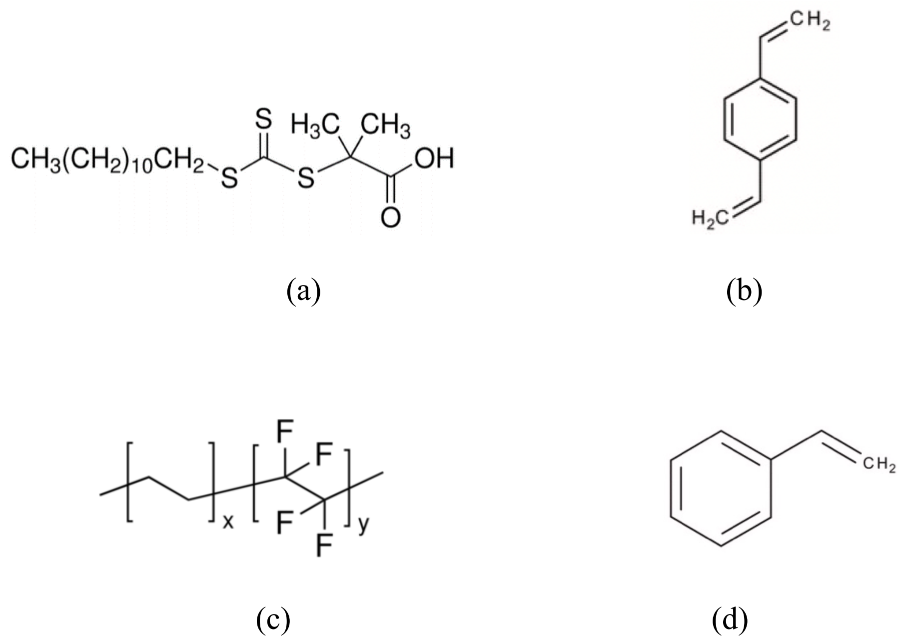
Free radical polymerization is extensively used in the synthesis of crosslinked polymers. However, it is impossible to control the polymer chains and the network structure formed by free radical polymerization. Therefore, controlled radical polymerization methods have been used in crosslinked polymer synthesis due to their advantages in controlling chain composition, structure, and functionality. In the literature, ATRP [93, 94], NMP [101, 102], and RAFT [103], which are among the CRP methods, have been carried out in the presence of crosslinking agents, and the effects of these methods on the obtained crosslinked gel structures were discussed.

The results obtained in these studies show that the crosslinking mechanism works differently in case of CRP methods. According to the proposed mechanism, fast-growing chains in conventional free radical polymerization are mostly intramolecularly crosslinked to form densely crosslinked microgels. The combination of different microgels forms a heterogeneous polymeric network structure. In RAFT polymerization, on the other hand, because of reversible chain transfer reactions, the chains grow slower and parallel to each other in length, thereby leading intermolecular crosslinking occurs more intensely than the intramolecular. As a result, a more homogeneous network structure is formed [98–100]. As an example, crosslinking in case of RAFT polymerization yields well-defined molecularly imprinted polymers that present higher molecular recognition values up to 40% compared to conventional FRP [107]. This study and others in the literature have shown that "well-defined" crosslinked polymeric structures will be obtained when using RAFT polymerization when irradiation is carried out in the presence of the crosslinker. In this way, it increases our belief that superior polymer electrolyte membranes may be obtained via radiation-induced RAFT polymerization technique. In the literature, the effects of RAFT polymerization on different polymerization types such as batch, solution, emulsion, suspension, and crosslinking mechanism in the case of using thermal and photoinitiators were investigated [97, 98, 100, 102]. However, there is no publication showing the effect of RAFT polymerization on the radiation-initiated crosslinking mechanism. Therefore, this thesis study also has important aspects in terms of crosslinking reactions carried out in a controlled manner via RAFT mechanism under a constant source of irradiation.

3. EXPERIMENTAL

3.1 Materials and Chemicals

In this thesis, poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), a fluorinated polymer film with reasonable price and high mechanical, thermal and chemical stability, was used as the main polymer substrate to be grafted. Polystyrene was grafted to this structure by RAFT polymerization under gamma irradiation (^{60}Co, 1 kGy/h, SANAEM, Sarayköy, Ankara). By grafting polystyrene to ETFE film in the presence of the crosslinker DVB and then sulfonation of samples obtained from both sets, two different membrane structures were attained. Monomer (styrene, ≥99%) and crosslinker (divinylbenzene, DVB) were purchased from Sigma-Aldrich. The inhibitors in monomer and crosslinker were removed by passing them through the active basic alumina (Sigma Aldrich) column. 2- (dodecylthiocarbonothioylthio) -2-methyl propionic acid (DDMAT, 98%, Sigma Aldrich) was used as the RAFT agent. The RAFT agent is reportedly suitable for the controlled polymerization of styrene, and it is commercially available [109].



(a) (b)

(c) (d)

Figure 3.1 Chemical structures of the RAFT agent (DDMAT) (a), crosslinker (DVB) (b), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE) (c) and the monomer (styrene) (d)

Toluene (Sigma-Aldrich) was used as a solvent in grafting of ETFE films. Also, it has been used to rinse the ETFE films.

3.1.1. Preparation of Polystyrene grafted Poly(ethylene-*alt*-tetrafluoroethylene) Films (PS-*g*-ETFE)

ETFE, the base substrate polymer in grafting, is a 25 µm thick film offered by DuPont (Circleville, United States) under the trade name of Tefzel® 100LZ. These films were provided by Dr. Günther G. Scherer (Paul Scherrer Institute, PSI, Switzerland). ETFE was chosen as the base polymer because it exhibits high mechanical strength and cost-effectiveness compared to other fluorinated polymers and is suitable for obtaining a high degree of grafting at low irradiation doses. ETFE has been used frequently due to its advantages mentioned in PEM research in recent years [104, 105]. ETFE film was washed in pure acetone and ethanol and dried in the furnace at 60 °C until it reached constant weight before grafting studies.

ETFE films, the first weight of which is weighed, in the reaction solution containing RAFT agent (DDMAT), crosslinker (DVB), monomer (styrene), and solvent (toluene), were degassed under N_2 gas for 10 minutes in glass flasks, followed by irradiation under ^{60}Co gamma source with 1 kGy h^{-1} dose rate at room temperature. ETFE films with approximately 1cm x 2cm were used in grafting experiments (some samples were placed in larger sizes for conductivity studies and chemical stability tests. In this case, the amount of solution was also increased at the same ratio. In chemical stability tests, membranes with the same properties were used by cutting).

At the end of certain irradiation periods, ETFE films taken from the gamma source were washed by shaking in toluene till constant weight. After all the non-grafted polymer was removed from the ETFE film by washing the films using toluene and regularly changing the solvent, the films were subsequently dried in the oven to constant weight. The degree of grafting (DG, wt%) was calculated gravimetrically using the following equation:

$$\mathrm{DG,\%} = \frac{\mathrm{W_f - W_i}}{\mathrm{W_i}} * 100 \qquad \text{Equation (1)}$$

W_i (g) is the initial mass of non-grafted ETFE film, W_f (g) is the final mass of grafted ETFE copolymer film.

At the end of the irradiation, the unreacted monomer (styrene), crosslinker (DVB), and solvent (toluene) were evaporated first in the fume hood and then in a vacuum oven. The amount of polymer formed in the reaction vessel was calculated. Total monomer conversion was calculated by summing the amount of polymer grafted into ETFE films and the amount of polymer formed in the reaction medium (non-grafted). Note: DVB is a crosslinker and can be considered also as a monomer. It is added to the chain as a monomer and should be included in the conversion calculation.

$$\text{Overall Conversion} = \frac{(\mathrm{W_f} - \mathrm{W_i}) + \mathrm{W}(Polymer_{\mathrm{Homo}})}{\mathrm{W}_{monomer}} \mathrm{x100} \qquad \text{Equation (2)}$$

In a previous study [9], the optimal monomer/RAFT agent ratio was determined as 700, this ratio was therefore kept the same here too. The theoretical molar mass was differentiated by changing the monomer conversion. Since monomer conversion is a parameter of the reaction time (or irradiation dose), ETFE copolymer structures with different molar mass and degrees of grafting were obtained by changing the irradiation time.

One of the most important parameters that will determine the properties of PS-*g*-ETFE films is the % grafting yield. The % grafting yield was calculated by comparing the weight of the ETFE film before and after grafting. The parameters mainly effect % grafting yield are:

- The concentration of monomer (Styrene) and crosslinker (DVB) in the solution and their molar ratio, and
- The total amount of absorbed radiation dose

Grafting studies on ETFE film were carried out under different conditions by changing the above two parameters.

3.1.2. Sulfonation of Polystyrene grafts to yield Poly(styrene sulfonic acid) (PSSA) grafted ETFE membranes (PSSA-*g*-ETFE)

Polystyrene grafted ETFE films were placed in dichloromethane and left for 2 hours to allow swelling of the grafted polystyrene layers. The ETFE-*g*-PS films were sulfonated using 10% vol. chlorosulfonic acid in dichloromethane at room temperature for 2 hours, and a poly (styrene sulfonyl chloride) structure was formed. They were then rinsed with deionized water and stirred for 2 hours in 1 M NaOH solution. Again, the films rinsed several times with deionized water and stirred in 1 M H_2SO_4 for 3 hours and poly (styrene sulfonic acid) functional groups were obtained. As a result of these processes, the ETFE-*g*-PSSA films (called *membranes* hereafter) were obtained to use as PEMs. All mentioned steps are summarized in Fig-3.2 [55].

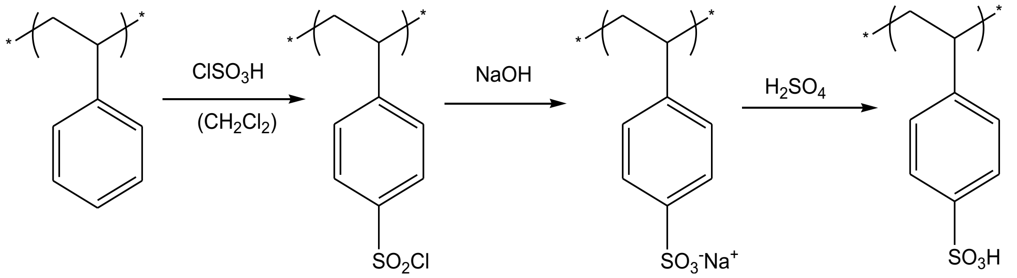


Figure 3.2 Steps of the Sulfonation Reaction of Polystyrene

Experimental studies regarding the grafting and sulfonation are summarized in Figure *3.3*. Before and after sulfonation, characterizations of the membranes were carried out. Then, under optimally selected conditions, larger membranes with a surface of approximately 5 cm^2 were prepared, and their proton conductivity and chemical stability were investigated.

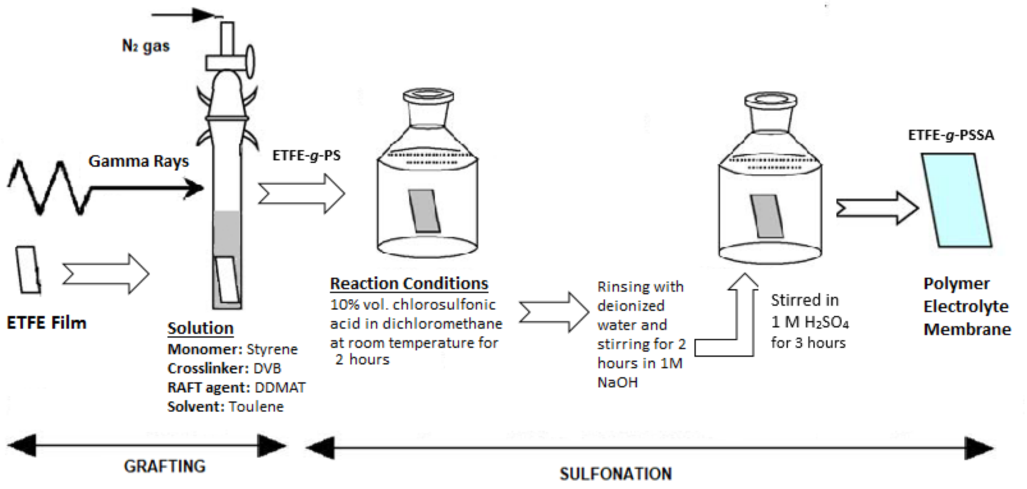


Figure 3.3 An exemplary experimental synthesis method

An exemplary experimental synthesis method in Figure 3.3 and a summary of the analyzes carried out afterwards are as follows.

- The synthesized copolymers were characterized by different experimental techniques (FTIR, XPS, AFM, SEM, SEM-EDX, TGA, DMA, CA) before and after sulfonation.
- Membrane properties such as proton conductivity and ion-exchange capacity (IEC) have been investigated.

Technical details and the intended use of the instruments employed for characterizations (ATR-FTIR, XPS, AFM, SEM-EDX, TGA, DMA, CA and IEC) are briefly summarized below:

3.2. Equipment

3.2.1. ATR FTIR Spectroscopy Analysis

Using Perkin Elmer Spectrum One FT-IR spectrometer and ATR module, the IR spectra of the pristine ETFE film, PS-grafted ETFE films and the sulfonated membranes in the range of 400-4000 cm^{-1} were measured. 32 scans were taken and analyzes at 4 cm^{-1} resolution.

3.2.2. X-ray Photoelectron Spectroscopy (XPS)

Thermo Scientific Al K-Alpha-Monochromated High-Performance XPS Spectrometer was used. Measurements were carried out by applying a vacuum of approximately 3×10^{-8} mBar. The transition energy of electrons for detailed scanning was 30 eV, and for general scanning, 150 eV.

3.2.3. Atomic Force Microscopy (AFM)

Morphological feature studies to be carried out with AFM, morphological characteristics of the grafted samples were determined. AFM measurements were carried out in tapping mode and air atmosphere using Bruker Nanoscope V Atomic Force Microscope. Morphological feature studies to be carried out with AFM, morphological characteristics of the grafted samples were determined.

3.2.4. Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM EDX)

SEM images were taken using FEI Quanta 200 FEG microscope. Using the Supra 35VP Leo SEM EDAX device and applying a 15 kV accelerating voltage, the sulfur atom profile in the cross-sections of the samples was examined. The samples were frozen in liquid N_2 before SEM EDX analysis and then cut with scissors to obtain a flat section.

3.2.5. Thermogravimetric Analysis (TGA)

Thermal degradation properties of polymers were investigated using a Perkin-Elmer PYRUS Thermogravimetric Analyzer and TA Instruments DMA (Pyris 1 TGA). The analyzes were carried out in an N_2 atmosphere, between 25-700 °C, with a heating rate of 10 °C/min. Thermal stability of films and membranes was investigated using TGA curves and the first derivatives of these curves.

3.2.6. Dynamic Mechanical Analysis (DMA)

The mechanical properties of pristine ETFE, ETFE-*g*-PS films with different grafting percentages, and the membranes obtained by their sulfonation were examined by TA Instruments Q 800 DMA device. Measurements were performed in pull mode, applying an oscillating motion (strain) with an amplitude of 20 μm and a frequency of 1 Hz, at a heating rate of 2 ºC/min, and between 30ºC and 200 ºC. The glass transition temperatures (T_g) of the samples were found with the peak maximum of the tan δ curve.

$$tan\delta = \frac{E''}{E'} \qquad \text{Equation (3)}$$

Where, E′ is the loss module of the polymer and E" is the storage module.

3.2.7. Ion Exchange Capacity (IEC)

The theoretical ion-exchange capacities were calculated as shown in the Equation (4), considering that one sulfonic acid group is attached to each styrene unit. Here, DG indicates the degree of grafting, M_{St}, is the molar mass of styrene (104.15 gmol^{-1}), and M_{SSA} indicates the molar mass of styrene sulfonic acid (184 gmol^{-1}).

$$\mathrm{IEC_{teo}} = \frac{\mathrm{DG}}{\mathrm{M_{St}} + \mathrm{DG} * \ \mathrm{M_{SSA}}} \qquad \text{Equation (4)}$$

To calculate the experimental ion exchange capacities, three samples for each grafting percentage were immediately weighed after drying in the furnace at 60 °C for one day. The dry membrane masses were found. Then, the films placed in 10 mL of 1 M NaCl solution were kept for 24 hours, and the ion exchange was completed. Titration was performed using standardized 0.01 M NaOH, and experimental ion exchange capacities were calculated using the following equation. Three samples were averaged.

$$\mathrm{IEC_{exp}} = \frac{\mathrm{M_{NaOH}} + \mathrm{V_{NaOH}}}{\mathrm{W_{memb}}} \qquad \text{Equation (5)}$$

where M_{NaOH} given in the equation is the molarity of NaOH used in titration, V_{NaOH} is the volume of NaOH used, and W_{memb} is the membrane mass.

Membranes are highly hygroscopic due to the presence of the sulfonic acid groups. Therefore, it would be inaccurate to calculate the percentage of sulfonation gravimetrically. Instead, it is more accurate to calculate the ratio between the experimental ion exchange capacity, and the theoretical ion exchange capacity.

3.2.8. The Water Uptake or Swelling Measurements

The water uptake, φ_w is found as the mass of water absorbed by the membrane divided by the dry weight of the membrane, according to the following equation.

$$\varphi_w = \frac{W_\xi - W_d}{W_d} \qquad \text{Equation (6)}$$

In this equation, W_ξ is the weight of the water-swollen membrane and W_d is the dry weight of the vacuum-dried membrane at 80 ^{o}C.

The hydration number, λ, of the membrane is the number of water molecules per sulfonic acid site and defined according to the following equation (7) [12]:

$$\lambda = \frac{n(H_2O)}{n(SO_3H)} = \frac{\varphi_w}{IEC} x \frac{1}{M(H_2O)} \qquad \text{Equation (7)}$$

4. RESULT AND DISCUSSION

Gamma-induced RAFT-mediated controlled graft copolymerization of styrene in the presence of DVB crosslinker and ETFE as the base polymer was performed under inert atmosphere. The grafting technique using radiation has been chosen because it provides some advantages over other methods:

- This method allows inexpensive polymer films to be modified without requiring stringent reaction conditions. Also, there is no need for reshaping at the end of the synthesis. Based on fluorinated polymers such as ETFE, it is possible to easily obtain stable membranes with different properties by radiation-induced grafting method.
- Changing the dose of radiation applied during the reaction makes it possible to easily adjust the membrane properties, such as the degree of grafting (DG) of the films, water uptake capacity and proton conductivity.
- The radiation-induced grafting method is a suitable technique for conducting simultaneous crosslinking reactions as well as polymerization. If grafting is carried out in the presence of a crosslinker, increased chemical and mechanical stability can be achieved due to simultaneous crosslinking reactions.
- The radiation-initiated grafting method can be applied in harmony with RAFT mechanism, so that the grafting can be carried out in a well-defined manner. RAFT polymerization used for grafting provides structural control. In this thesis, the advantages of structural control achieved by RAFT polymerization and ease of modification by radiation-induced grafting technique are combined to obtained well-defined PEM structures. As a result of this facile combination, membranes with high proton conductivity could be prepared following the sulfonation of polystyrene grafts on ETFE.

Fluorinated and highly crystalline polymers such as ETFE are insoluble in any common solvent or monomer. In addition, such polymer structures either show no swelling behavior or swell very little. The grafting of such polymers under radiation takes place with the "*grafting front mechanism*" proposed by Chapiro in 1962 [112]. According to this mechanism, polymerization starts first on the surface to be grafted, then continues through the cross-section with the swelling of the grafted surface layers in the polymerization solution and the diffusion and grafting of the monomer into the swollen inner layers. In this way, grafting progresses layer by layer towards the entire interior (cross-section). Since radicals are formed inside the polymer film as well by irradiation, the entire polymer cross-section can be grafted.

When the radicals formed in the polymer film under irradiation meet the monomer molecules, the grafting begins on both film surfaces. The grafting, which starts from both surfaces and progresses to the inner parts with diffusion, meets each other in the middle of the membrane section. Thus, the whole of the film, including the inner parts, is grafted [113]. This mechanism is known to work similarly in the presence of a crosslinker. Because of the parallel running of grafting and crosslinking throughout the entire membrane cross-section, it is possible to obtain membranes that are grafted as a whole and have the desired mechanical and thermal properties.

During the grafting, some portion of monomer (styrene) forms polystyrene gel structure with the crosslinker DVB in solution, while the rest is grafted onto the ETFE film. Polymers grafted onto and inside ETFE film are covalently bonded to the main polymer backbone and cannot be broken off and analyzed. However, non-grafted polymers formed in solution are good replicas of the grafted polymers [56]. Therefore, a thorough understanding of what happens during the synthesis requires examining the gels formed in solution as well as the grafted ETFE films. The characteristics of these non-grafted polymers before and after gelation have been the subject of Ovalıoğlu's master thesis and studied in detail [114]. In this current study, the structure of the gels formed in solution was not examined, but the characterization and performance of the obtained films were focused.

The main purpose of the thesis is to synthesize crosslinked polystyrene grafted ETFE films by radiation-induced RAFT polymerization in the presence of DVB for the first time in the literature and to examine their proton carrying capacity following their sulfonation. Although polystyrene is considered an indispensable polymer choice for full cell studies due to its promise of high levels of sulfonic acid group, it suffers from chemical stability, making it necessary to develop alternative solutions. The most accessible and plausible solution is to crosslink polystyrene to increase its chemical and mechanical strength. Therefore, the use of DVB in this thesis is one of the main motivations.

4.1. Optimization of Grafting Conditions

Although DVB is a crosslinker in this study, it is also considered a monomer because it is included in the grafted chains. Consequently, grafting experiments were carried out using different concentrations of both styrene and DVB. Also, the total radiation dose absorbed was varied. For this purpose, grafting studies were carried out using three different DVB amounts (3.5%, 5%, and 10%, v/v). These DVB ratios were chosen to form the MSc. thesis of Ovalıoğlu to examine the copolymerization and simultaneous grafting of styrene and DVB [114]. Styrene concentration was varied in the range of 10-80 % (v/v), while a total absorbed radiation dose between 0.7 – 11.3 kGy was employed. 30% (v/v) styrene was used in grafting studies carried out by varying DVB amount, as it was a mean value. In the case where the amount of styrene was changed, 3.5% DVB was used. This amount of DVB was chosen because it is predicted that by using less DVB, gelation will be slower and thus diffusion of monomers across the cross-section of ETFE film will be more feasible/easy. The results of all these trials were given in Table 4.1.

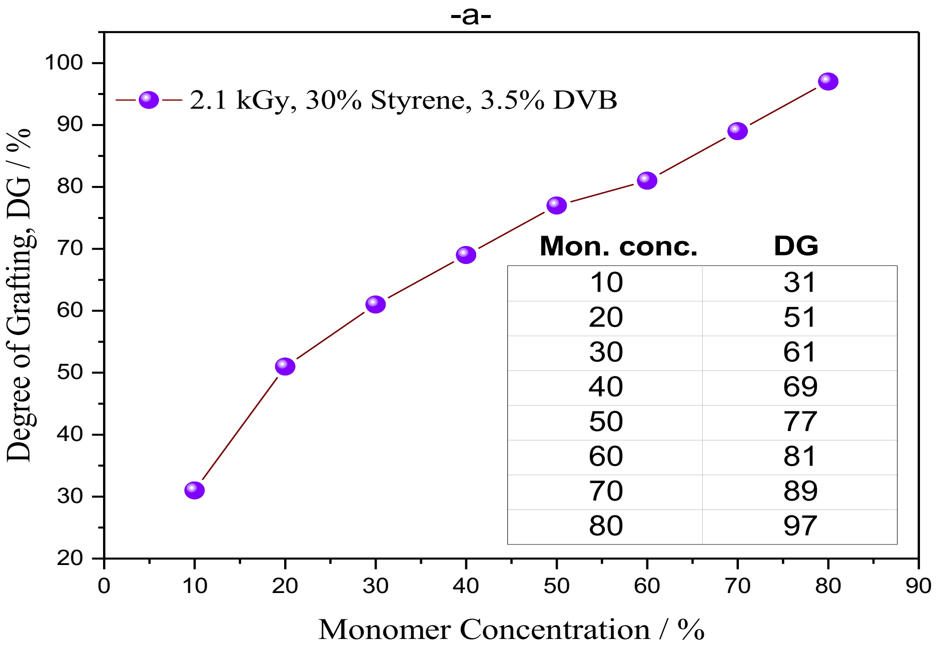
Table 4.1 Radiation-induced grafting of styrene in the presence (entities 1-28) and absence (entity 29) of DVB. [St]/[DDMAT]=700, ETFE (0.01 g), solvent: toluene, dose rate: 1 kGy/h.

Entity No.	DVB, %	Rad. Dose, kGy	Monomer Conc.	DG, %
1	3.5	0.7	30	15
2	3.5	1.0	30	31
3	3.5	2.1	10	31
4	3.5	2.1	20	51
5	3.5	2.1	30	61
6	3.5	2.1	40	69
7	3.5	2.1	50	77
8	3.5	2.1	60	81
9	3.5	2.1	70	89

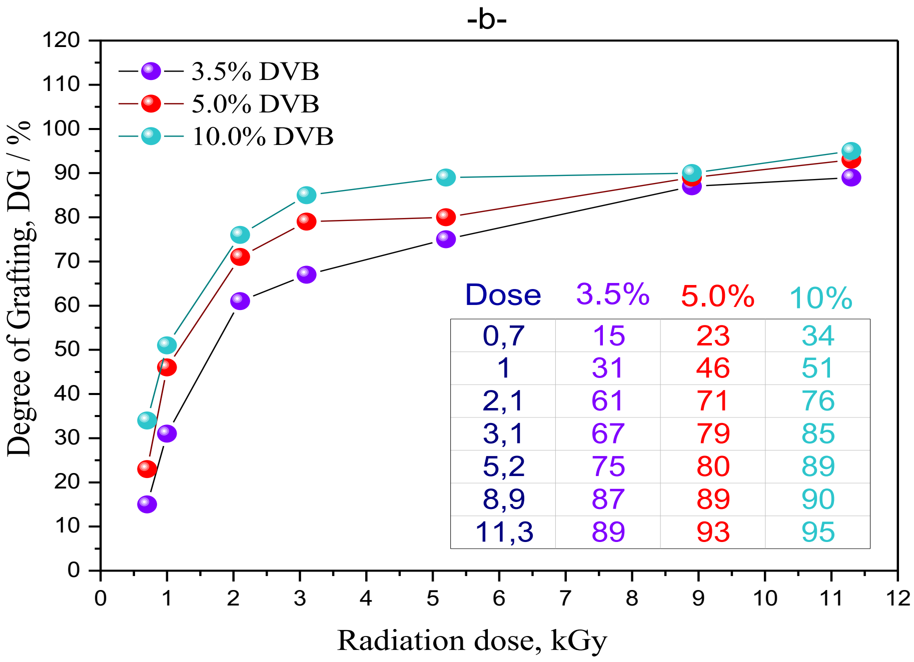
10	3.5	2.1	80	97
11	3.5	3.1	30	67
12	3.5	5.2	30	75
13	3.5	8.9	30	87
14	3.5	11.3	30	89
15	5	0.7	30	23
16	5	1.0	30	46
17	5	2.1	30	71
18	5	3.1	30	79
19	5	5.2	30	80
20	5	8.9	30	89
21	5	11.3	30	93
22	10	0.7	30	34
23	10	1.0	30	51
24	10	2.1	30	76
25	10	3.1	30	85
26	10	5.2	30	89
27	10	8.9	30	90
28	10	11.3	30	95
29	0	11.3	30	53

In order to better follow the trends obtained as a result of the experiments carried out, the data in Table 4.1 were presented in related figures. Using entities 3-10 in Table 4.1., Figure 4.1(a) is plotted showing the change in degree of grafting of ETFE film in the presence of DVB crosslinker and DDMAT RAFT agent depending on the monomer concentration. In Figure 4.1(b), as a function of absorbed radiation dose, degrees of grafting were presented separately for three DVB concentrations using the entities in Table 4.1. Each data used in these graphs is also presented as an internal table in the figures for the sake of simplicity of following the data.

From the results presented in Figure 4.1(a), it is seen that the degree of grafting (DG) increases with the monomer concentration. The DG ranged from 31% to 97%, with the monomer variation between 10% and 80%. The higher the DG, the more styrene groups are obtained in grafting to carry protons following the sulfonation. Therefore, the increase in DG causes an increase in membrane properties such as proton conductivity, water uptake capacity, and ion exchange capacity. Although this is perceived as a desirable situation, the increase in degree of grafting may cause some disadvantages as well. For example, with the increase of DG, the integrity of membranes begins to deteriorate. Polystyrene is a fragile polymer at room conditions with a glass transition temperature of around 100°C. Therefore, at high degrees of grafting (approx. 50-60%), membranes become fragile and begin to show phase separations. Cloudy heterogeneous regions visible to naked eye appear at grafting degrees above approximately 50% in ETFE film, which is transparent before grafting. For this reason, the optimum degree of grafting is reported as about 50% in previous studies. Although an increase in membrane properties is observed by increasing DG, membranes are not practically usable. Therefore, as shown in Figure 4.1(a), monomer concentrations above 30% are unnecessary in real applications as the DG attained is quite high. The use of less monomer is also a reason for preference from an economic point of view.



Mon. conc.	DG
10	31
20	51
30	61
40	69
50	77
60	81
70	89
80	97



Dose	3.5%	5.0%	10%
0,7	15	23	34
1	31	46	51
2,1	61	71	76
3,1	67	79	85
5,2	75	80	89
8,9	87	89	90
11,3	89	93	95

Figure 4.1 a) Degree of grafting (%) versus monomer concentration (%) for the radiation induced grafting of styrene (30%, v/v) from ETFE film in the presence of crosslinker (DVB, 3.5%) and RAFT agent (DDMAT) at an absorbed radiation dose of 2.1. kGy. b) Degree of grafting (%) versus absorbed radiation dose (kGy) using three different DVB concentration (3.5%, 5%, 10%, v/v) at a styrene concentration of 30% (v/v). [St]/[DDMAT]=700, ETFE (0.01 g), solvent: toluene

In Figure 4.1(b), using 30% (v/v) styrene, results of grafting carried out in the presence of three different of DVB concentrations (3.5%, 5%, and 10%) were presented as a function of radiation dose, hence reaction time. As can be seen in this figure, DG at low radiation doses shows a rapid increase in all three DVB concentrations. After about 3 kGy radiation dose, the increase in DG slows down significantly, and then it is almost stabilized. The monomer and DVB in the reaction medium are consumed over time. By increasing the radiation dose, the degree of grafting does not change significantly after a while and reaches its equilibrium value. Increasing the amount of DVB increases the amount of monomer conversion as expected. Therefore, by increasing DVB concentration, the amount of polymer grafted onto ETFE has increased in line with this expectation.

As shown in Figure 4.1(b), PS-*g*-ETFE copolymer with 31% degree of grafting was obtained at only 1 kGy irradiation using 3.5% DVB. In previous studies [114], it was determined that gels synthesized by RAFT polymerization in the presence of 3.5% DVB showed controlled growth up to much higher radiation doses. For this reason, as we could achieve the desired level of grafting with such a low radiation dose in the presence of 3.5% DVB, the optimum DVB amount was determined as 3.5% in this thesis. Since the optimum monomer ratio was chosen as 30% before, 1 kGy radiation dose, at which we reached the sufficient degree of grafting (around 30%), was decided as the optimum radiation dose. Therefore, unless stated otherwise, all further experiments of this thesis were carried out in the presence of 30% styrene and 3.5% DVB with a monomer/RAFT agent molar ratio of 700 and a radiation dose of 1 kGy (the degree of grafting of ETFE-*g*-PS films synthesized under these experimental conditions are presented in the purple column in Figure 4.1(b)). Please note that since the same degree of grafting could not be obtained each time in repeated experiments and the synthesized films were not of sufficient size for all tests, films with different DGs are used in the characterizations carried out in the later parts of this thesis. Also, it is worth to mention that although the grafted films are shown as ETFE-*g*-PS, it should be kept in mind that the DVB crosslinker has also participated in the composition of PS chains through the formation of crosslinks. In the later parts of this thesis, ETFE-*g*-PS notation is preferred for the graft copolymer structures for convenience. A final note on Table 4.1, as expected, lower DG was obtained from the synthesis carried out in the absence of DVB (entity 29), and this sample was saved for use in post-membrane property tests.

4.2. Structural Characterization of Polystyrene Grafted ETFE Films Synthesized in the Presence of DVB by Radiation-induced RAFT Polymerization and Membranes Obtained by Sulfonation of These Films

4.2.1. ATR-FTIR Spectroscopy

First, the FTIR method was used for the characterization of synthesized films (Figure 4.2). The FTIR spectra below show the results of pristine ETFE, 61% PS grafted ETFE, and membrane obtained by the sulfonation of this PS-*g*-ETFE film. Since samples having degrees of grafting below 50% are more critical for the determination of membrane properties, these samples were kept for further tests, and samples with higher DGs (61%

for FTIR) were used in structural characterizations. In the ATR-FTIR spectrum of ETFE, characteristic peaks of asymmetric and symmetrical aliphatic -CH_2- stretching are seen as weak peaks at 2976 and 2880 cm^{-1} region. –CH stretching gives severe peaks in FTIR for apolar structures. Therefore, these peaks are quite severe in non-polar structures. However, the electron-withdrawing property of F atoms in the structure of ETFE increases the polarity of the partial -CH bonds. In addition, it causes the intensity of the stretching bands belonging to these peaks to decrease [115]. Strong characteristic peaks of -CF_2 stretching and -CH_2 deformations are seen between the 1500-500 cm^{-1} region. At approximately 1453 and 667 cm^{-1}, wagging and scissoring deformation peaks of CH_2- are in the spectrum. Sharp peaks originating from –CF_2 groups appear in the range of 1000-1300 cm^{-1}. In the spectrum of the 61% PS grafted ETFE-*g*-PS sample, characteristic peaks of aromatic polystyrene are seen in the range of 2700 - 3200 cm^{-1}. The C-H deformation bands of the mono-substituted benzene ring that appear at approximately 696 and 756 cm^{-1} prove PS binding to the structure. In the spectrum of the ETFE-*g*-PSSA copolymer obtained by sulfonation of this structure, the wide absorption band between 3000-3600 cm^{-1} is due to the –OH groups in the water molecules held by sulfonic acid groups. This band proves spectroscopically that the structure has turned into a hydrophilic state. The broadband detected in the wavenumber range of approximately 1600-1700 cm^{-1} is due to -OH structures in the sulfonic acid groups. The stretching peaks of the sulfated benzene ring and the vibration peaks originating from the –SO_3 groups were observed at 1004 and 1135 cm^{-1}, respectively. C-H deformation peaks in the disubstituted benzene ring appear at 832 and 774 cm^{-1}. All these spectroscopic results indicate that the synthesis has been successfully carried out.

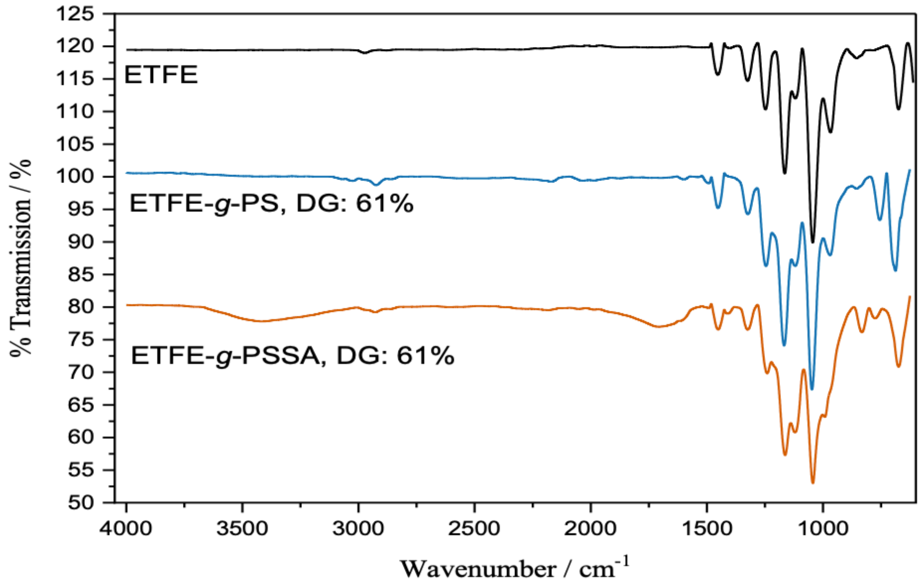


Figure 4.2 ATR-FTIR spectra of non-grafted (pristine) ETFE, 61% PS grafted ETFE film (ETFE-*g*-PS), and the sulfonated membrane of the same film (ETFE-*g*-PSSA)

4.2.2. X-ray Photoelectron Spectroscopy (XPS) Analysis

XPS is one of the primary analysis methods used for surface characterization. The XPS results of non-grafted ETFE, 61% PS grafted film (ETFE-*g*-PS), and sulfonated membrane of the same DG (ETFE-*g*-PSSA) are presented in Figure 4.3 below. When the wide-range surface scan spectrum of ETFE film is examined, F 1s peak is seen at approximately 689 eV binding energy (BE). The peak around 290 eV corresponds to C 1s (Figure 4.3). The atomic percentages calculated from F 1S and C 1S peaks show that these elements are present in the structure at approximately 53.5% and 46.1%, respectively. The molar ratios of ethylene and tetrafluoroethylene monomers for the consecutive ETFE copolymer should be 50% -50%, so the amount of C and F elements should be equal. However, many commercial ETFE polymers are not perfectly sequential, so this ratio ranges between 60-40% [115]. The ethylene-tetrafluoroethylene mole ratios of the ETFE sample used in this thesis were found to be approximately 46% and 54%, respectively.

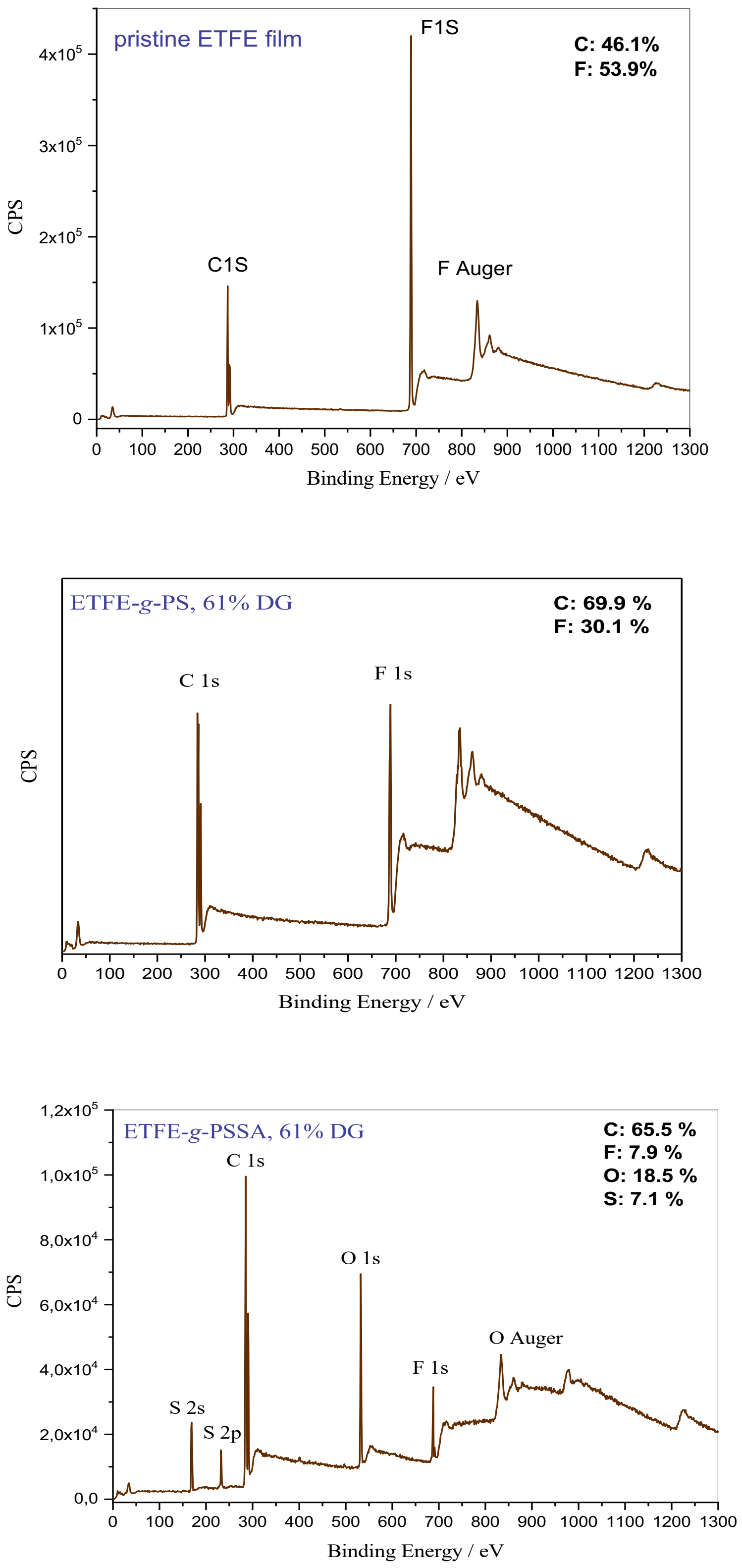


Figure 4.3 Surface wide-scan XPS spectra of non-grafted ETFE, 61% PS grafted (ETFE-*g*-PS) film, and sulfonated membrane of the same film (ETFE-*g*-PSSA)

When the XPS spectrum of 61% (w/w) PS grafted ETFE-*g*-PS film was examined, there was a significant increase in C element due to PS chains added to the structure, and its percentage increased from 46.1% to 69.9%. As a consequence of this increase, the amount of F element decreased to 30.1%. When the surface analysis of the ETFE-*g*-PSSA membrane with 61% degree of grafting obtained by sulfonation of this film is examined, it is seen that O (15.7%) and S (4.3%) atoms are added to the structure. The presence of O atoms at about 532.2 eV and S atoms at 168.5 eV confirms the sulfonic acid (-SO_3H) groups. The percentage of F atoms in the structure decreased to 7.9% and C to 65.5%. A slight decrease in the amount of C atoms (from 69.9% to 65.5%) due to sulfonation indicates a relative decline due to the increase in other atoms. In fact, the decrease in the amount of C atoms would have been expected to be more pronounced due to the abundant -SO_3H groups added to the structure. However, possibly sulfonated PS chains are pushed through free volume regions via electrostatic interactions, which enriches the surface with grafted chains. If there were no enrichment by the graft chains on the surface, the addition of O and S atoms to the structure after sulfonation would have resulted in a more significant decrease in the amount of C atoms.

XPS is a method that not only gives the elemental composition of the surface but also provides essential information about the chemical environment of the elements. For this, the core-level C1s and O1s spectra of the samples were examined in detail. In the pristine ETFE structure, the CH_2 and CF_2 groups are expected to exhibit two C1s spectra of almost equal intensity, appearing at approximately 285.9 and 290.7 eV, respectively. Consistent with this expectation, two peaks are visible in the spectrum of the ETFE-*g*-PS sample with a 61% degree of grafting (Figure 4.4, left). However, in addition to these two ETFE-induced peaks, a third and a rather severe C1s band is appeared at higher binding energy region. This peak belongs to the aromatic C=C and -CH structures of PS added to the structure [116]. This result proves that PS was grafted to ETFE film. The O1s spectrum of the ETFE-*g*-PSSA membrane obtained by sulfonation of this film can be divided into two components. The first of them corresponds to the severe peak of S=O groups at 532 eV. The O-H groups cause the less intense peak seen at 533.3 eV. The ratio of the areas of these two peaks to each other is approximately 2:1, which is an expected result when considering the structure of -SO_3H groups [117].

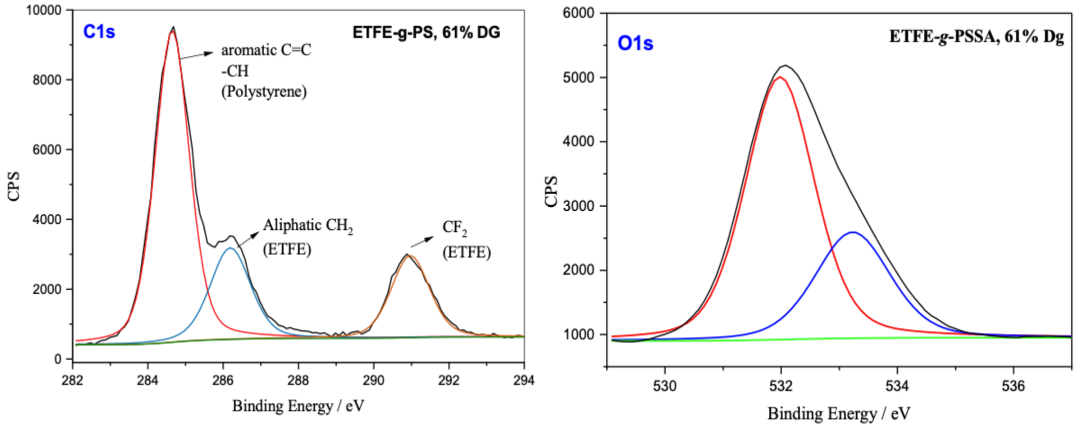


Figure 4.4 Core-level C1s and O1s XPS spectra of ETFE-*g*-PS (DG: 61%) and sulfonated membrane of the same film (ETFE-*g*-PSSA)

Similar XPS analyzes were performed also for ETFE-*g*-PS films and sulfonated membranes with different DGs, and surface elemental composition of each sample as determined by XPS are presented in Table 4.2.

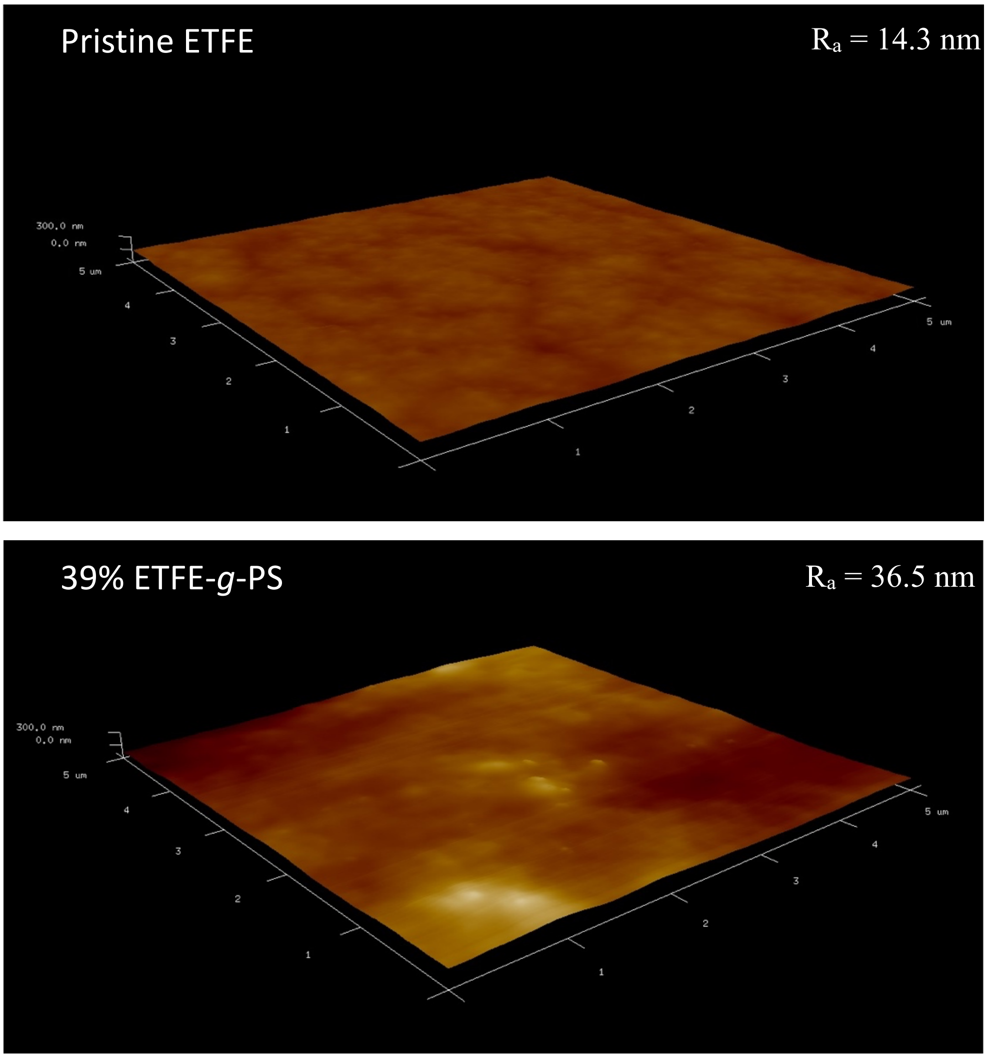
Table 4.2 Surface elemental atomic compositions obtained by XPS survey wide scans of pristine ETFE film, ETFE-*g*-PS films, and sulfonated membranes with different degrees of grafting.

Samples	F (%)	C (%)	O (%)	S (%)
ETFE	53.9	46.1	-	-
% 39 ETFE-*g*-PS	38.6	61.4	-	-
% 61 ETFE-*g*-PS	30.1	69.9	-	-
% 87 ETFE-*g*-PS	19.5	80.1	-	0.4
% 39 ETFE-*g*-PSSA	19.7	60.3	15.7	4.3
% 61 ETFE-*g*-PSSA	7.9	65.5	18.5	7.1
% 87 ETFE-*g*-PSSA	1.7	66.3	22.3	9.7

When the values presented in Table 4.2 are examined, it is seen that the percentage of C atoms in the structure increases significantly while the amount of F atoms decreases, as expected, by grafting of polystyrene to ETFE. In ETFE-*g*-PS sample with an 87% degree of grafting, some S atoms originating from the sulfur-containing RAFT chain-end moieties are observed. This is an essential clue that the synthesis mechanism proceeds through the steps of RAFT polymerization. In the sulfonated ETFE-*g*-PSSA samples, S and O atoms are detected in the XPS results due to the addition of -SO_3H groups to the structure. The amount of these two elements increases as the degree of grafting increases.

4.2.3. AFM Analysis

The surface morphologies of pristine ETFE, PS grafted films (ETFE-*g*-PS) with different DGs (39%, 61% and 87%) along with a sulfonated membrane (ETFE-*g*-PSSA) of 61% PS grafted film were characterized by AFM. AFM images and the roughness values (R_a) calculated are presented in Figure 4.5.



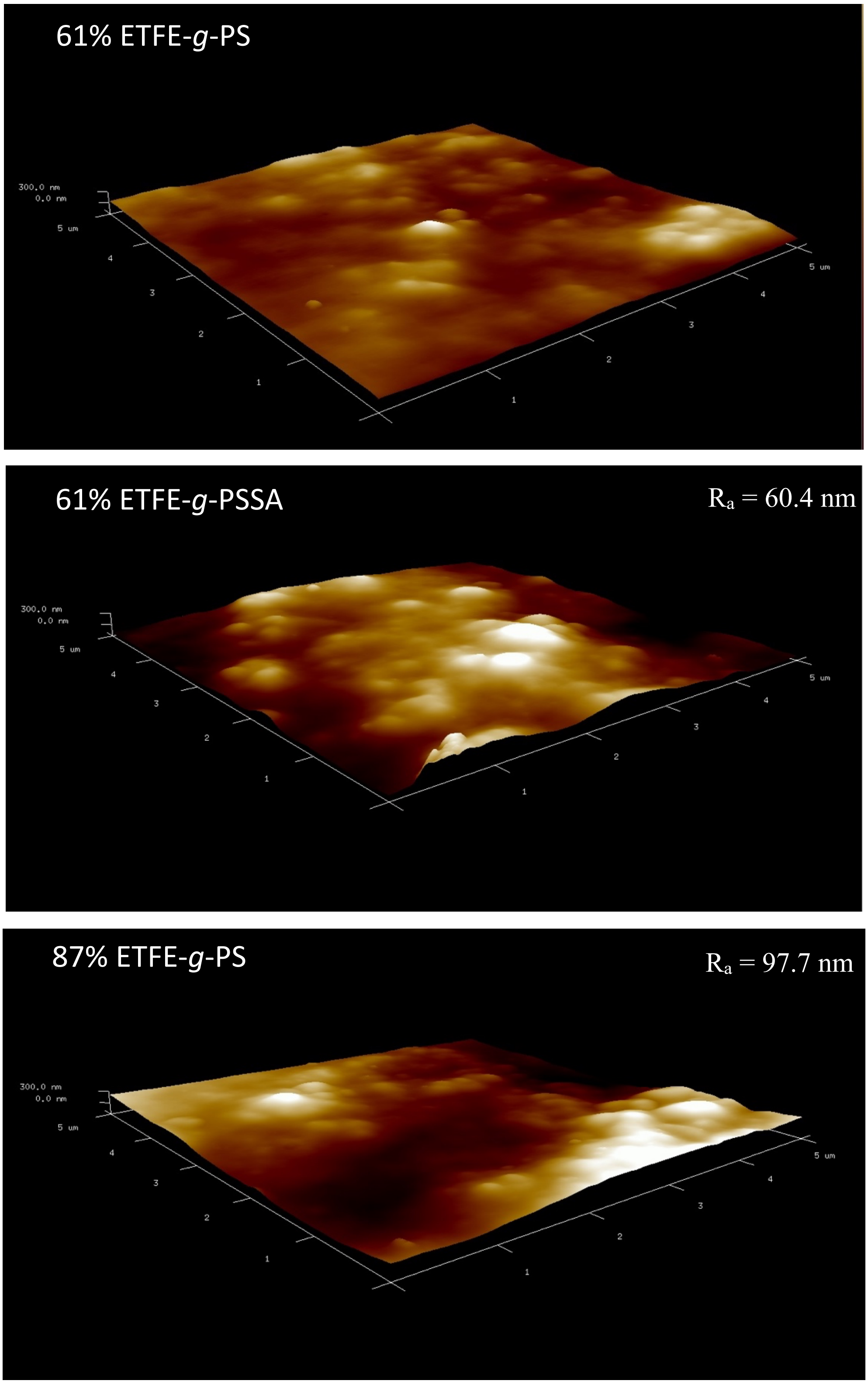


Figure 4.5 AFM images and roughness values (R_a) of pristine ETFE, PS grafted films (ETFE-*g*-PS) with different DGs (39%, 61% and 87%) and sulfonated membrane (ETFE-*g*-PSSA) of 61% PS grafted film.

When the AFM images are examined, it is seen that surface roughness increases as a result of grafting. The increase in roughness with increasing degree of grafting confirms the morphological changes on the surface. ETFE is insoluble in any solvent and only slightly swollen. However, after PS grafting, the film becomes swellable in suitable solvents and the film increases in size [110]. Growth in size causes bending and inflection in the film surface. In addition, grafting onto the surface itself is a cause of morphological changes. When comparing the AFM images of 39%, 61%, and 87% PS grafted samples, the roughness increases with increasing DG. In the AFM image of 87% grafted ETFE-*g*-PS sample, prominent PS clusters are noticeable. This indicates that at very high DGs, the surface loses its homogeneity, and PS clusters begin to form on the ETFE surface. This heterogeneity can be noticed even with the naked eye in samples with the degree of grafting of over 60%. The sulfonation causes a small change in surface morphology and roughness. Ra increases slightly from 53.9 to 60.4 after sulfonation of grafted ETFE-*g*-PS film with 61% DG. It indicates that both ETFE and PS do not undergo a severe morphological change during the sulfonation reaction.

4.2.4. Contact Angle Measurements

Contact angle measurements also confirmed the surface properties of grafted films and sulfonated membranes. As shown in Figure 4.6, the water contact angle of pristine ETFE is nearly the same as the PS grafted ETFE films with all degrees of grafting. The polystyrene-grafted films (ETFE-*g*-PS) do not show significant changes in water contact angle (CA) with the degree of grafting, as reported earlier in the literature [47]. Since both ETFE and PS are hydrophobic structures, a significant change in CA is not expected after grafting. However, a significant decrease in CA is observed due to the hydrophilic character added to the structure after sulfonation. Scherer et al. observed that the water CA decreased to 32° after sulfonation for a DG of 82% in non-crosslinked membranes; however, for crosslinked structures the water CA decreased less as crosslinking limits the mobility of chain segments [118]. In our study, the water CA values decreased with increasing degrees of grafting in sulfonated membranes, and it is 53.4° at a DG of 87%. These results are consistent with the literature.

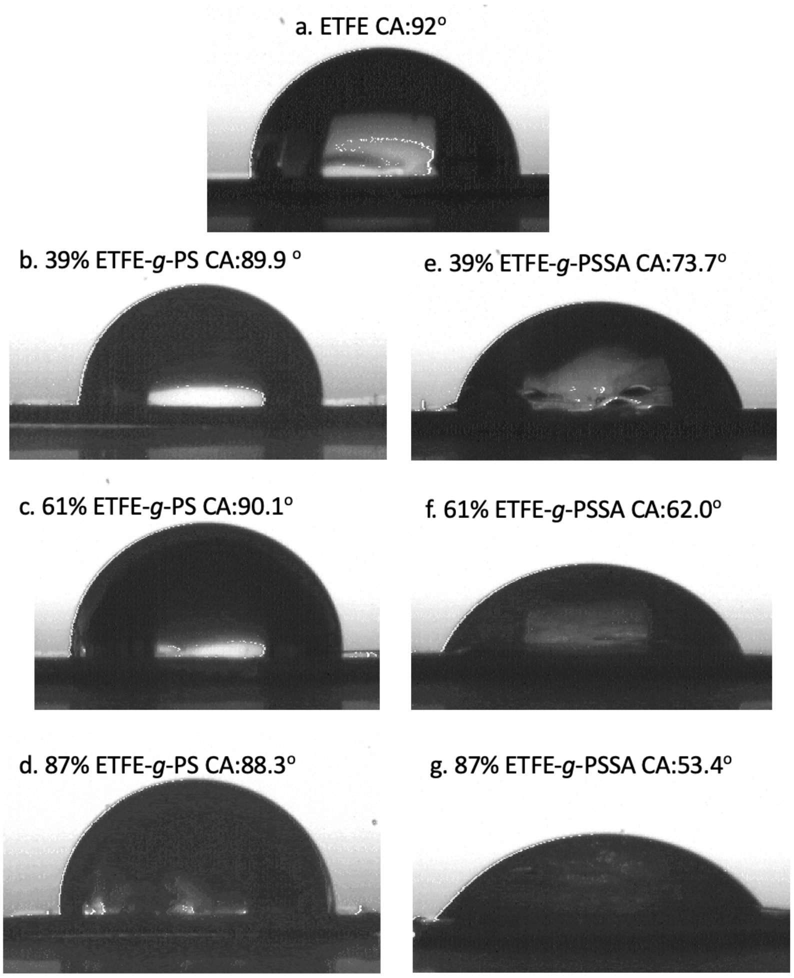


Figure 4.6 Water Contact Angle (CA) images of pristine ETFE, ETFE-*g*-PS with 39%, 61% and 87% degrees of grafting and their sulfonated ETFE-*g*-PSSA membranes

4.2.5. SEM-EDX Analysis

For proton transmission to be achieved across the membrane cross-section, PS must be grafted *not only on the surface* but also through the inner parts of the membrane. SEM images and SEM-EDX mappings for S element for the surface of PS grafted ETFE film with DG of 61% and the sulfonated membrane of this film are presented in Figure 4.7(a) and Figure 4.7(b), respectively. As can be seen form the S element mapping in Figure 4.7(a1), a small number of red dots corresponds to the S atoms in the RAFT-moieties at the chain ends of PS grafted to ETFE. After the sulfonation of this film, there was a significant increase in the amount of S atoms on the entire surface. Moreover, S atoms show a homogeneous distribution on the surface, which indicates that the grafting and subsequent sulfonation took place in a homogeneous manner. As mentioned before, for a successful proton conductivity, grafting must have taken place across the entire membrane cross-section so that protons can be transported from one side of the membrane to the other via -SO_3 groups. The cross-sectional SEM and SEM-EDX analysis of the membranes was carried out for ETFE-*g*-PSSA with DG of 61% to examine whether grafting has occurred along the entire membrane cross-section. As can be seen Figure 4.7(c) below, a significant amount of S atoms was detected in the cross-section of ETFE-*g*-PSSA sample. The sulfur-rich areas marked by red dots are spread homogeneously over the entire cross-section. This indicates that not only the surface of the membranes is grafted by PS, but also their interior along the entire cross-section. In addition, the homogeneous distribution of S atoms indicates that the grafting takes place homogeneously also in the cross-sectional area.

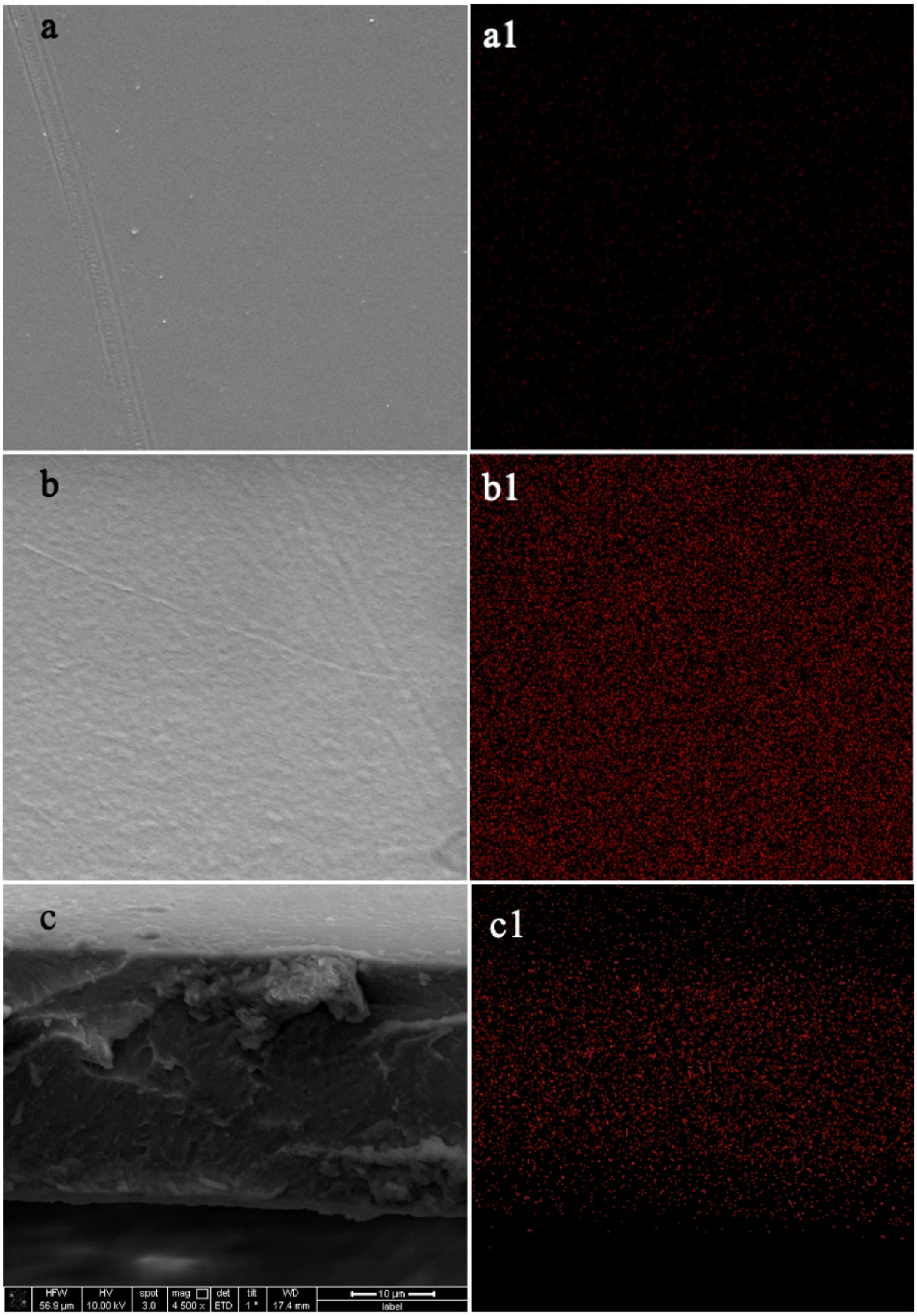


Figure 4.7 SEM image of (a) the surface of PS grafted ETFE film (ETFE-*g*-PS, DG: 61%), (b) surface of the sulfonated membrane (ETFE-*g*-PSSA, DG:61%), and (c) cross-section of the sulfonated membrane (ETFE-*g*-PSSA, DG:61%). Figures a1, b1 and c1 show the distribution of S atoms in the corresponding SEM image.

4.2.6. TGA Analysis

TGA is an effective method to examine the structure and thermal stability of grafted films. In Figure 4.8, TGA curves of pristine ETFE film and sulfonated membranes (ETFE-*g*-PSSA) with DGs of 39%, 61%, 87% are presented. From the thermograms, it has been observed that pristine ETFE film has a single-step degradation profile; the degradation starts at approximately 440 °C, and there is almost no mass loss up to this temperature. It is seen that the decomposition reaches its maximum at around 505 °C. As can be seen from the TGA results of PSSA grafted membranes, the degradation shows a multi-step profile. It is understood that membranes with different degrees of grafting are highly hydrophilic because of sulfonic acid groups in their structures. Each membrane loses about 15% of its initial mass up to about 200 °C. It is understood that ETFE films, which do not normally contain water in their structures, absorb significant amount of water after PSSA grafting. However, while the amount of water in the structure is expected to increase with the degree of grafting, it is an unexpected result that all membranes contain almost the same amount of water, and it is incompatible with the water uptake capacity tests presented in the following parts. This may be because a standard drying process was not applied to the membranes prior to TGA; possibly easily removable water molecules were evaporated from the structure in random amounts. It was reported that the degradation patterns of ETFE-*g*-PSSA membranes depend on the drying procedure applied before the TGA measurements [13].

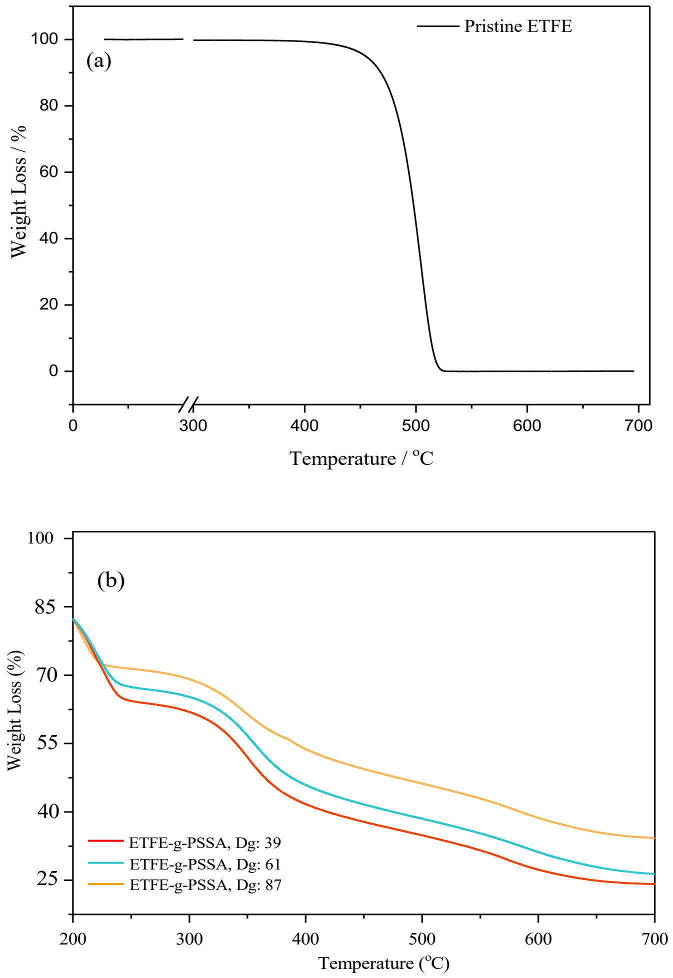
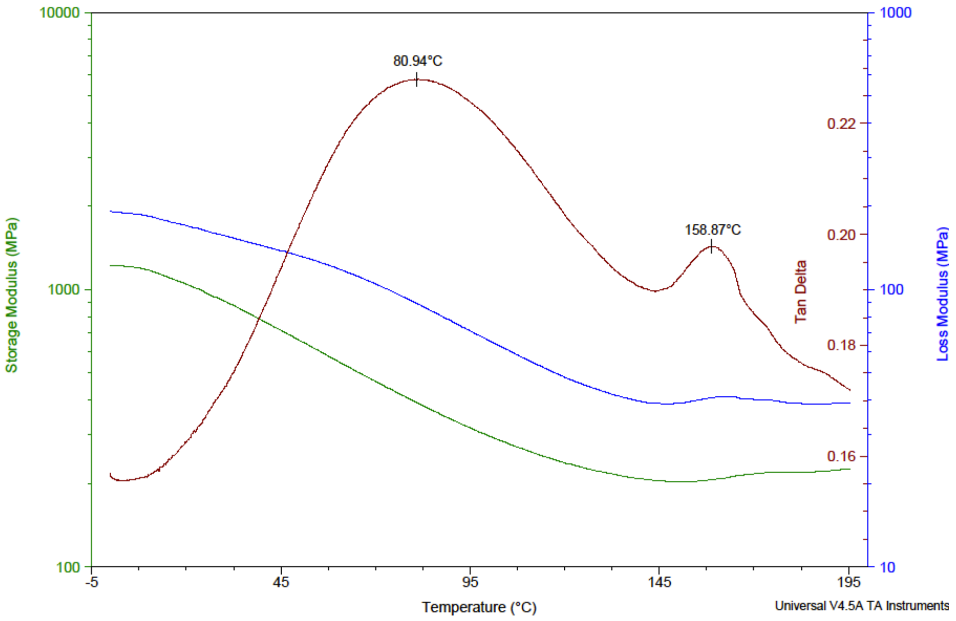


Figure 4.8 TGA thermograms for (a) pristine ETFE and (b) ETFE-*g*-PSSA samples with different degrees of grafting

ETFE-*g*-PSSA membranes appear to exhibit a three-step degradation profile. The first degradation step at approximately 250-300 °C is followed by the second one known as desulfonation, in which sulfur oxides are separated from the structure. Afterward, ETFE's main degradation pattern (at about 550 °C) is seen. This degradation profile is compatible with the literature [9]. In a study by Youcef et al., similar initial and maximum decomposition temperatures and tree-step degradation profiles were reported for crosslinked ETFE-based membranes [13]. In addition, at the end of the thermal degradation of pristine ETFE film, there is almost no mass left (Figure 4.8(a)). In contrast, some mass remains after decomposition of sulfonated samples. The amount of residue increases with increasing DG, as expected, and reported in literature [119].

4.2.7. DMA Analysis

DMA is an effective method for determining the glass transition temperatures of polymers. The maximum peak values seen in the tan δ curves result from α-relaxation and give the polymer's glass transition temperature *(T_g)*. From the DMA results in Figure *4.9*, it is seen that ETFE-*g*-PS samples show T_g at two different temperatures. The T_g value of pristine ETFE film has been reported as about 135 ºC [120]. The T_g value of polystyrene is around 100 ºC, and it can also be observed in the lower temperature ranges up to 50-60 ºC depending on its molecular weight [121].



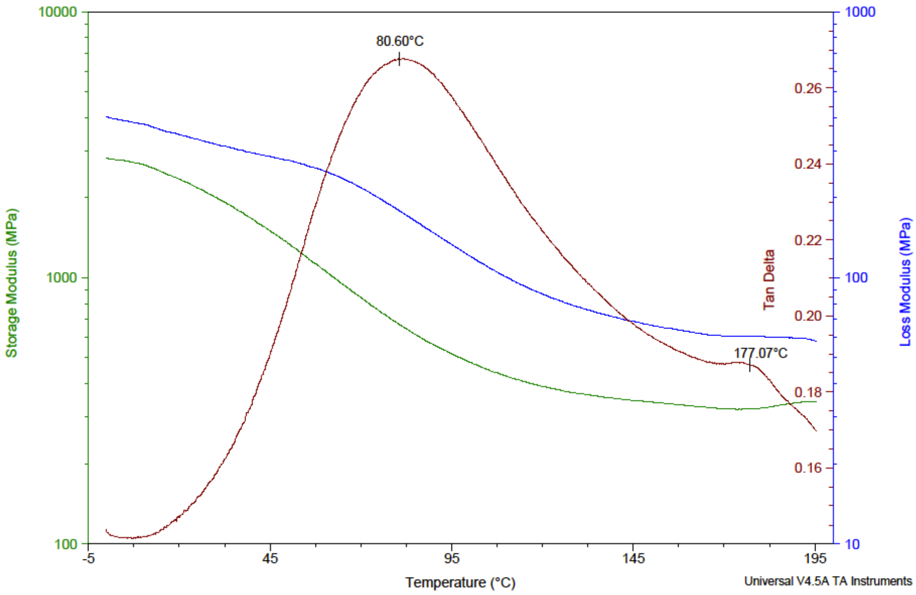


Figure 4.9 Tan δ, storage modulus and loss modulus changes of ETFE-*g*-PS films with DGs of 39% (top) and 87% (bottom) against temperature.

As shown in the DMA results presented in Figure *4.9*, the first glass transition temperature seen at approximately 80 ºC belongs to the PS chains grafted into the structure. Both ETFE-*g*-PS films with DGs of 39% and 87% exhibit similar T_g temperatures for PS. The second T_g value that appears at higher temperatures belongs to the ETFE unit in the structure. While the T_g value of pristine ETFE is about 135 ºC, the T_g values increased after grafting. The grafting of PS to ETFE chains restricts the mobility of the ETFE chains, causing an increase in T_g value. The T_g value of ETFE-*g*-PS with 87% grafting (about 177 ºC) is higher than the T_g of 39% PS grafted ETFE sample (about 158 ºC) since the mobility of ETFE chains is further restricted by increased grafting in the structure.

4.3. Evaluation of Membrane Properties of ETFE-*g*-PSSA Membranes

4.3.1. Ion Exchange Capacity (IEC)

The easiest and most effective way to get information about the number of acidic groups with ion exchange capacity in the structures of membranes is to measure the ion exchange capacity (IEC) value. An indirect but reliable estimate of proton conductivity can be made with IEC measurements [44]. The IEC values calculated using the equations given in experimental section were plotted against degree of grafting in Figure *4.10*.

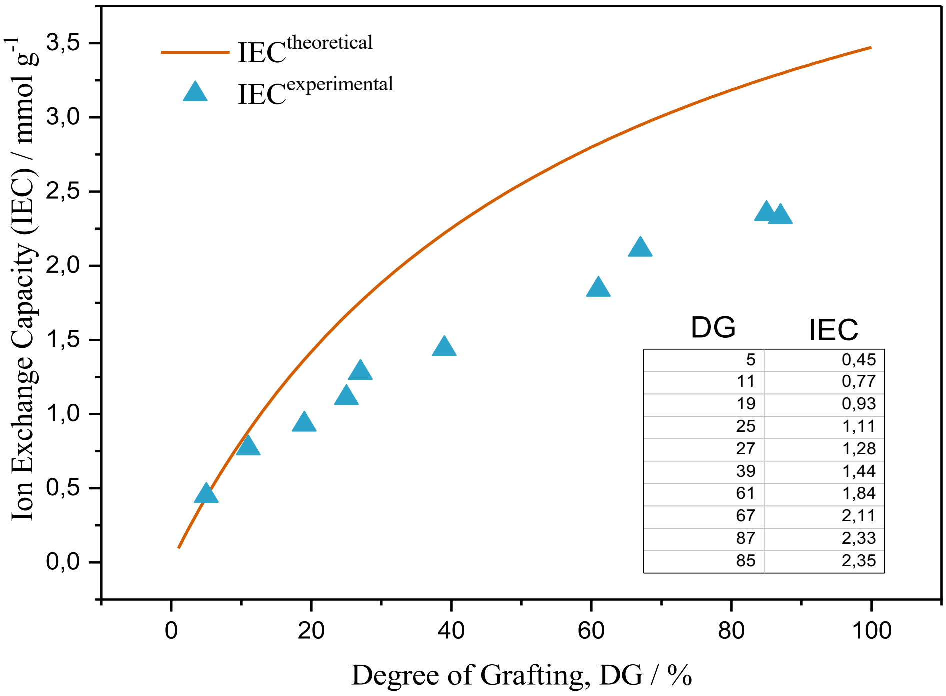


Figure 4.10 Variation of the ion exchange capacity (IEC) with the degree of grafting of ETFE-*g*-PSSA membranes (5-87%)

Sulfonation percentages calculated by comparing experimental and theoretical IEC values are presented in Table 4.3. When this table and Figure 4.10 are examined, it is seen that the experimental IEC and the theoretical IEC value are quite compatible with each other at low degrees of grafting. This initial agreement between the theoretical and experimental IEC values weakens with increasing degree of grafting, and the sulfonation percentage is fixed in the range of approximately 60%-70%, except for some deviations. The deviations may be due to the inability of the membranes held in the NaCl solution to complete the ion exchange [44].

It is also seen from Table 4.3 that the ion exchange capacity increases with the degree of grafting as the number of sulfonic acid groups in the membrane structure increase with DG. As can be seen from the data in this table, at high degree of grafting, the IEC value reaches sufficient values for a suitable fuel cell membrane. For instance, the IEC value of commercially used Nafion-112 is 0.91 mmol/g [122]. For membranes synthesized within the scope of the thesis, this value could be exceeded by only a 19% grafting.

Table 4.3 Experimental and theoretical ion-exchange capacities and sulfonation percentages of ETFE-*g*-PSSA membranes with different degrees of grafting (5-87%)

DG, %	**IEC_{teo}**	**IEC_{exp} (mmol/g)**	**Percentage of Sulfonation (%)**
5	0.442	0.43	97.2
11	0.885	0.77	87.0
19	1.367	0.93	68.0
25	1.667	1.11	66.5
27	1.757	1.28	72.9
39	2.219	1.44	64.9
61	2.821	1.84	65.2
67	2.948	2.11	71.6
85	3.262	2.35	72.0
87	3.294	2.33	70.7

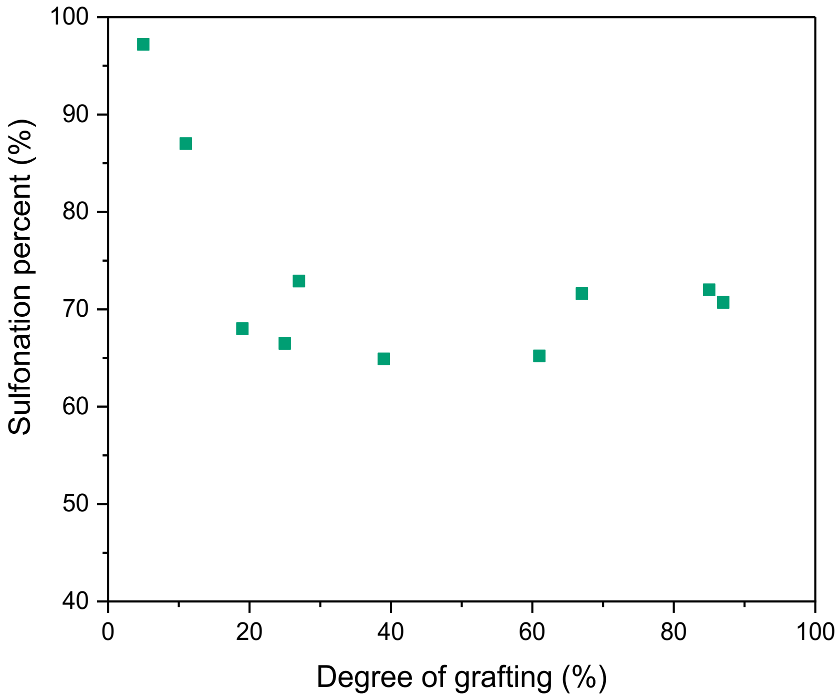


Figure 4.11 The variation of the sulfonation (%) as a function of degree of grafting of ETFE-*g*-PSSA membranes (5-87%)

4.3.2. Water Uptake Capacity Evaluation

One of the important parameters affecting the performance of membranes is water uptake capacity. This value gives information about the amount of water absorbed by the membranes, and therefore the number of hydrophilic groups the membrane has. The hydration number is calculated by the water uptake capacity and gives the number of water molecules held by the membrane per sulfonic acid group. Since this value determines the mobility of protons within the membrane, it is an important parameter affecting the conductivity of the membranes in the structure of perfluoro sulfonic acid [123].

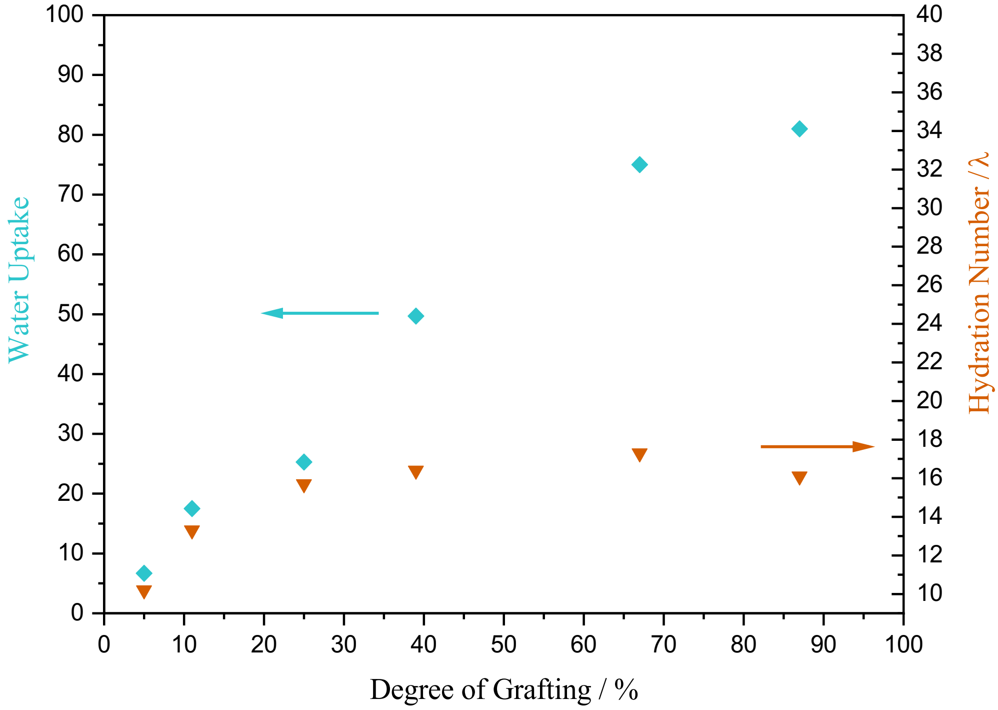


Figure 4.12 Variation of water uptake capacity and hydration number of ETFE-*g*-PSSA as a function of degree grafting (DGs: 5%, 11%, 25%, 39%, 67%, and 87%)

The hydration number and water uptake capacity values of perfluoro sulfonic acid membranes increase with degree of grafting because the amount of hydrophilic sulfonic acid group in the structure increases with the grafting. The results presented in Figure 4.12 are consistent with this expectation. When the literature is examined, it is seen that the water uptake capacity is 33.5%, and the hydration number is 18 for the Nafion 112 membrane, which is widely used commercially [7, 12]. Some experimental results and literature comparisons are presented in Table 4.4. The water uptake capacity of the membranes synthesized within the scope of the thesis is relatively high (varying between 6.7% and 81%). The main reason for this is thought to be the high-water uptake of the crosslinked polymeric network along the entire membrane cross-section. However, the number of water molecules (hydration number) retained per repeating unit reached 17.3 at most, although the amount of water uptake increased. In addition, it is seen from Figure 4.12 that after a certain degree of grafting (about 40%), the hydration value does not increase, even slightly decreases. This is somehow different from previously reported membranes obtained by grafting only polystyrene to ETFE film without DVB [9]. We compared the water uptake capacity, IEC and hydration number of the membranes synthesized in our study with those of similar membranes reported before and commercial Nafion samples in Table 4.4. The DG values and membrane properties of PEMs reported in the literature vary widely as the experimental conditions such as dose rates, absorbed doses, concentrations, temperatures, etc., are quite variable. However, it is possible to say that the values we obtained in this thesis are similar or partially superior when compared with those previously reported and especially with commercial Nafion samples.

Table 4.4 Comparison of our results with other works reported on ETFE-*g*-PSSA membranes synthesized by radiation-induced grafting method and commercial Nafion samples.

DG, %	DVB, %	IEC (mmol/g)	Water Uptake, wt%	Hydration number, λ	Ref.
25^a	*3.5*	*1.11*	*26.0*	*15.5*	*This thesis*
39^a	*3.5*	*1.44*	*51.0*	*16.0*	*This thesis*
67^a	*3.5*	*2.11*	*77.0*	*17.0*	*This thesis*
37^b	0	1.71	41.0	13.0	[9]
48^b	0	2.08	64.0	17.0	[9]
25.6	0	1.71	33.9	10.8	[10]
36	0	1.51	30.0	-	[11]
45-55	0	2.15-2.45	-	11.0	[52]
25.8	5	1.71	21.9	7.0	[10]
51.7	10	2.22	14.2	3.55	[12]

30.4	10	1.66	10.3	3.44	[10]
24.1	10	1.74	14.1	4.6	[10]
24.9	20	1.45	7.8	3.0	[10]
Nafion 112	0	0.91	33.5	18.0	[10]
Nafion 105	0	1.00	51.0	28.0	[11]
Nafion 117	0	0.89	37.0	23.0	[11]

[a]ETFE-g-PSSA in this thesis by RAFT-mediated grafting of PS in the presence of DVB, [b] ETFE based PEM by RAFT mediated grafting of PS without DVB. All the other membranes were synthesized by conventional radiation-induced grafting method.

4.3.3. Proton Conductivity Evaluation

Proton conductivity value (σ, S cm^{-1}) was found using the following

Equation (6). In this formula, R (Ω) is the membrane resistance found by impedance measurements; A is the membrane cross-sectional area through which the current passes (cm^2), and L is the thickness of the membrane (cm). Approximately 2.5 x 2.5cm size sample is required for measurements. The results presented in the table below (Table 4.5) demonstrate the potential of the membranes to show high proton conductivity.

$$\sigma = \frac{L}{R * A} \qquad \text{Equation (6)}$$

Table 4.5 Membrane properties obtained in this thesis and their comparison with literature data and commercial Nafions

Entity No.	Sample DG, %	DVB, %	Thickness L/ µm	Ohmic Resistance ®/ mΩ cm^2	Conductivity (σ)/mS.cm^{-1}	Ref.
1	*25*[a]	*3.5*	*41.2*	*317*	*19.2*	*This thesis*
2	*39*[a]	*3.5*	*45.6*	*99.7*	*70.9*	*This thesis*
3	*45*[a]	*3.5*	*47.7*	*73.3*	*93.7*	*This thesis*
4	*67*[a]	*3.5*	*53.3*	*57.9*	*139.1*	*This thesis*
5	*53*[b]	*0*	*46.1*	*38.9*	*173.9*	*This thesis*
6	48[c]	0	47.3	31.86	148.2	[9]

7	36	0	90.0	250.0	43.0	[11]
8	25.6	0	25.0	-	102.0	[10]
9	25.8	5	25.0	95.0	62.0	[10]
10	24.1	10	25.0	-	26.0	[10]
11	24.9	20	25.0	-	16.0	[10]
12	18.2	10	25.0	113.0	41.0	[10]
13	34	0	145.0	130.0	108.0	[11]
14	Nafion 112	0	58.0	86.0	82.0	[12]
15	Nafion 105	0	210.0	220.0	51.0	[11]
16	51.7	10	39.0	83	41.0	[12]
17	45	5	50.0	-	70.0	[52]

[a]ETFE-g-PSSA prepared in this thesis by RAFT-mediated grafting in the presence of DVB, [b]ETFE-g-PSSA prepared in this thesis by RAFT-mediated grafting in the absence of DVB [c]ETFE based PEM by RAFT mediated grafting in the absence of DVB– literature data. All the other membranes were synthesized by conventional radiation-induced grafting method.

When the results in Table 4.5 are examined, it is seen that the membranes obtained show promising results. 45% and 67% grafted membranes showed higher conductivity than commercial Nafion 112 and Nafion 105 membranes. However, the proton conductivity of the membranes is reduced when DVB is used, although the degree of grafting is increased (compare entities 4 and 5). Also, a higher conductivity of 148.2 mScm^{-1} at a DG of 47% has been reported in the literature when DVB is not used, compared to our data obtained at a comparable DG (entity 3 Table 4.5) [9]. A higher proton conductivity at comparable DGs is quite expected when a crosslinker such as DVB is not used. In many previous studies it has been reported that proton conductivity is reduced in the presence of a network structure [10]. It is well known that a crosslinked networks will allow less material transfer by diffusion than a non-crosslinked polymer structure [124]. In case of a network structure, mass transfer becomes difficult, and proton conductivity is restricted. Despite the decrease in conductivity, crosslinking, on the other hand, increases mechanical and chemical strength of the membranes. Therefore, achieving an optimum balance between the inversely corresponding strength increase and the conductivity decrease is a key criterion for developing a membrane that truly rivals Nafion.

When the literature is examined, it is seen that the proton conductivity values of PEMs synthesized by similar methods vary in a wide range. The reason for this is not only the difference in experimental conditions but also the non-standard measurement methods and devices used. Nevertheless, it can be said that the membranes synthesized in this thesis show high conductivity compared to the results obtained in studies using relatively similar experimental methods. For instance, the highest proton conductivity of an ETFE membrane with PS DG of 45% was reported as 70 $mScm^{-1}$ [52]. In another study, the conductivity of the DVB-crosslinked PS grafted ETFE film with a DG of 51.7% was 41 $mScm^{-1}$ in another publication [12]. In all these previous works, conventional free radical polymerization was employed instead of RAFT polymerization. Considering the promising results, we have obtained, it can be concluded that the well-defined and uniform grafting profile obtained by RAFT mechanism provides the same graft features in every region of the membrane, so that "uninterrupted" proton conductivity across the entire membrane cross-section can be achieved.

4.3.4. Chemical Stability Test

The degradation mechanism of PEMs based on polystyrene sulfonic acid (PSSA) is generally built on the weakness of hydrogen in the alpha position of the styrene group [125]. The products of the degradation reaction of *para*-toluenesulfonic acid molecules in a highly reactive chemical medium such as H_2O_2 were investigated by Electron Paramagnetic Resonance Spectroscopy (EPR) in literature [125]. It was seen that alpha-hydrogen on the aromatic ring was very susceptible to break from the structure due to the attack of $^{\cdot}OH$ radicals. The degradation mechanism, which started with the rupture of these H atoms, continued with the radicals formed on the main polymer chain, and finally, the chain was broken (Figure 4.13). Although similar degradation mechanisms occur for membranes used in fuel cell construction, this degradation model cannot fully explain all the chemical degradation processes that occur for PSSA-based membranes and how degradation proceeds under fuel cell operating conditions.

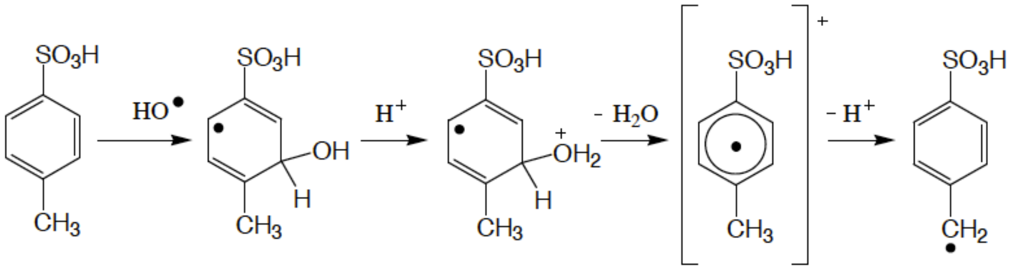


Figure 4.13 The basic degradation mechanism of PSSA-based membranes [125]

Chemical degradation is not the only problematic factor for Membrane Electrode Assemblies (MEAs); Physical factors also accelerate membrane degradation. Under fuel cell operating conditions, it has been determined that membranes become thinner, or pinhole-like formations occur in the structure over time [127, 128]. The initial physical properties of membranes are among the fundamental parameters that determine their thermal and mechanical stability. Therefore, parameters such as glass transition temperature, elongation at break and tensile strength are vital for the stability of membranes.

Tensile strength and elongation tests could not be performed within the scope of this MSc thesis. Standard "dog bone" pieces are required for these tests. However, the radiation source (Gamma cell) in which the experiments were carried out was not suitable for the preparation of such large samples. Even the sample size required for proton conductivity could hardly be prepared. Unfortunately, these mechanical tests could not be performed due to lack of access to a larger irradiation unit. Nevertheless, the results obtained from DMA and TGA provided important and promising clues for the performance and thermo-mechanical resistance of membranes. It should also be noted that standard tests used to measure physical characteristics such as glass transition temperature, elongation at break or tensile strength are performed in *dry* conditions. However, all these physical characteristics are affected by the hydration state of the membranes. The operation of proton electrode membranes in hot/*wet* conditions in a real application requires us to question the reliability of these measurements performed in hot/*dry* environments. There is also the complexity of establishing the relationship between the conditions under which membranes are characterized and fuel cells are operated. Therefore, given the overall scope of the study, the lack of tests for thermo-mechanical properties is not considered fatal.

Conventional fuel cell durability tests take more than a thousand hours, excluding design and component development. Therefore, fuel cell durability tests are not easy and are not done randomly. Mechanical tests performed for any polymer can be meaningless for a fuel cell membrane due to the differences between operating and measuring conditions, as noted earlier. Reliable protocols are needed for short-term tests to allow a faster assessment of the membrane's mechanical strength potential and durability in a fuel cell. There are many studies in the literature about different accelerated decomposition protocols (such as relative humidity cycle, start/stop cycles, Fenton reagent, etc.) [124]. One of the most practical and frequently used tests is the Fenton test. In a simpler version of the Fenton test, unlike the standard procedure, Fe^{+2} ions are not added to the medium and the degradation reaction was carried out under milder conditions. This chemical stability test is frequently used in the literature [29] by following the steps below:

- Membranes of approximately 0.5 x 0.5 cm in size were cut and oven-dried under vacuum.
- They were then weighed and kept in pure water overnight until equilibrium water absorption was obtained.
- Then the samples were placed in glass bottles containing 3% H_2O_2 aqueous solution (v/v) and kept at 60 ° C for different periods.
- At the end of each incubation period, a sample was removed from the solution, re-immersed in distilled water, and shaken for 24 hours.
- In the last step, the rinsed membranes were oven-dried under vacuum overnight and weighed a second time.
- Mass losses of the membranes were determined by comparing the initial and final mass measurements.

The data obtained from the chemical stability tests performed by following the above steps in order, are presented in Figure 4.14 for the samples with different DGs synthesized using varying amounts of DVB and applying the same radiation dose:

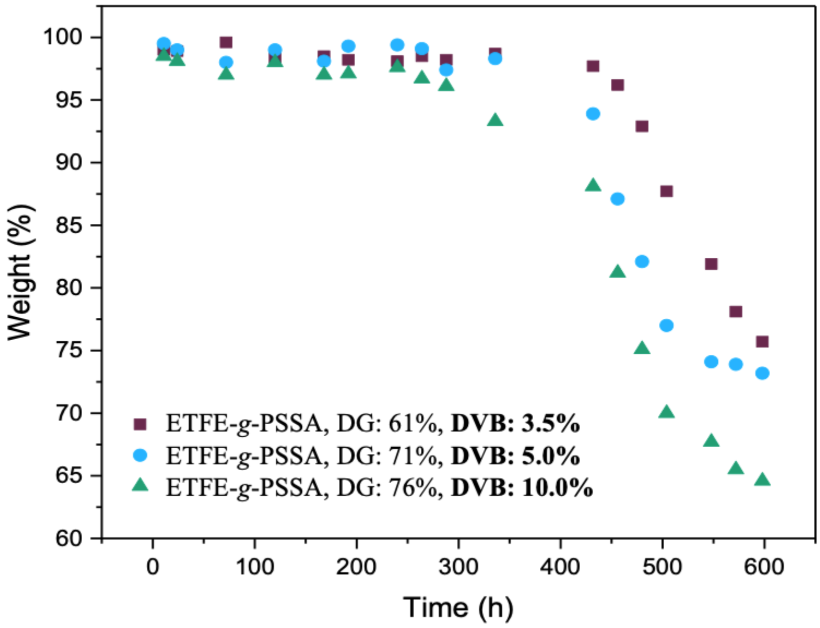


Figure 4.14 Chemical decomposition of ETFE-*g*-PSSA membranes with different degrees of grafting, synthesized using various DVB amounts at the same radiation dose (2.1 kGy) in a 3% H_2O_2 solution at 60 °C

The radiation dose used in grafting is highly effective on the mechanical and chemical properties of the membranes. Some degradation in membranes can be observed at high radiation doses. For this reason, samples with the same radiation dose were selected in order to make reliable comparisons in chemical stability tests. The way to obtain membranes with different DGs at the same radiation dose is to select samples in which the amount of DVB (crosslinker) is different. However, in this case, the only parameter that could change between the samples was not the amount of DVB, but also the degree of grafting as a dependent parameter. As expected, increasing the amount of DVB increases the amount of grafting. In brief, both the DVB amount and the degree of grafting change in the samples used for chemical stability tests make it somewhat difficult to interpretate.

When the results in Figure 4.14 are examined, a decrease in the chemical stability of the samples is noticed with the increase in the amount of DVB used, and hence with the increase in the degree of grafting. It is not expected at first glance to observe a decrease in chemical stability with an increase in the amount of DVB. However, increased DVB means more chain ends and shorter polymer chains between crosslinks. Since the chain ends are more prone to chemical decomposition, it is thought that increasing the amount of DVB facilitates chemical decomposition in the membranes [128]. As stated earlier, from the data presented in Figure 4.1, 3.5% DVB amount was optimized and used throughout the thesis. An unexpected benefit of using low DVB turned out to be increased chemical stability as presented in Figure 4.14. The high chemical stability achieved with the use of low DVB amount is a significant advantage.

On the other hand, it should also be noted that the use of DVB has an optimum value in terms of chemical stability as well, and not using it at all causes a very significant decrease in chemical stability. To test this, a similar experiment was carried out using the sample synthesized in the absence of DVB (Table 4.1, entity 29). The result of this test is shown in Figure 4.15.

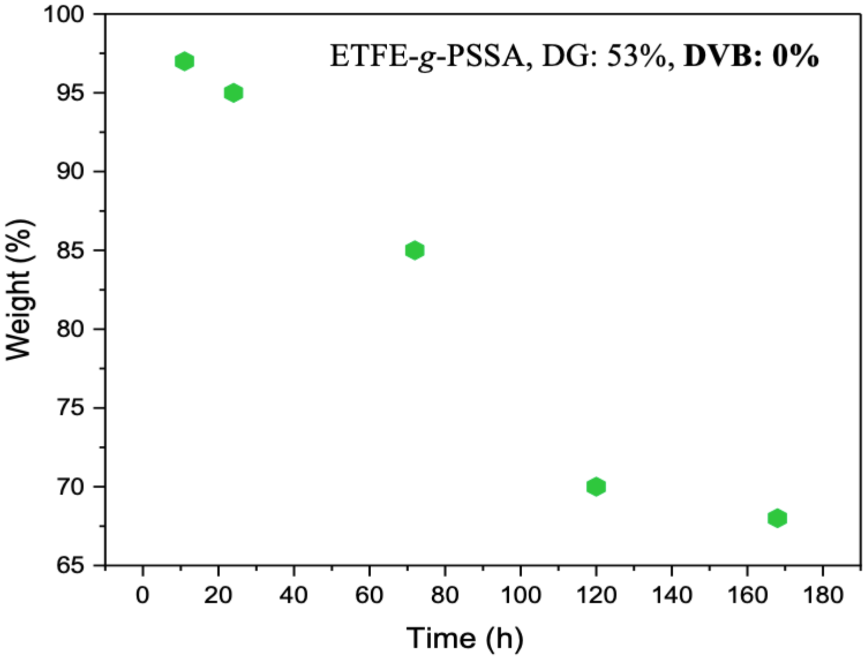


Figure 4.15 Chemical decomposition of ETFE-*g*-PSSA membrane at 53% degree of grafting, synthesized in the absence of DVB in 3% H_2O_2 solution at 60 °C.

As shown in Figure 4.15, the membrane synthesized without the use of DVB undergoes significant chemical decomposition after only around 100 hours. By comparison, samples synthesized in the presence of DVB show a similar level of degradation only beyond 400 hours, and almost no degradation in the first 300 hours. These observations agree with previous data, such as those reported by Nasef et al., where an increase in chemical stability in terms of mass loss from 55% (non-crosslinked) to 22% (crosslinked) was reported [128]. It is known that the chemical stability of proton exchange membranes is significantly increased by crosslinking while an optimization is required [29]. The results show that although there is a decrease in proton conductivity due to the use of DVB, crosslinking is a significant gain as there is a very substantial increase in chemical stability.

5. CONCLUSION

In this MSc thesis, well-defined PEMs were obtained by radiation-induced grafting of polystyrene to cost-efficient ETFE films by RAFT polymerization in the presence of a crosslinker (DVB) for the first time.

The membranes with various grafting degrees were characterized by ATR-FTIR, XPS, SEM-EDX, AFM, Contact Angle, TGA and DMA techniques. These extensive characterizations were used to confirm the existence of grafted PS chains in copolymer compositions and the success of the subsequent sulfonation. The results obtained from these techniques provided important results in terms of showing the positive impacts of radiation-induced RAFT polymerization method in terms of structural homogeneity and membrane properties. Especially when proton conductivity is taken into consideration, it is seen that promising results are obtained compared to previous data in the literature. It is also remarkable to note that the synthesized PEMs exhibited higher proton conductivity than many of their alternatives, including commercial Nafion samples. Considering the high proton conductivity of the membranes obtained and the specificity of the method applied, RAFT polymerization may be suggested as an efficient alternate experimental pathway to be used for the synthesis of well-defined PEMs, offering a unique synthesis approach compared to its counterparts in the literature.

The results obtained within the scope of the thesis are briefly summarized below:

- PEM was obtained for the first time in the literature by grafting of polystyrene to inexpensive ETFE films by radiation-induced RAFT polymerization in the presence of a crosslinking agent (DVB). Compared to PEMs synthesized by conventional methods in literature, unique PEMs with superior properties, especially in terms of proton conductivity, were synthesized thanks to the structural control and homogeneity achieved by the RAFT mechanism.
- The films and membranes with various degrees of grafting were characterized by ATR-FTIR, X-ray photoelectron, SEM-EDX, AFM, TGA, DSC, and DMA techniques.

- It is seen that the degree of grafting increases with the monomer concentration. The DG ranged from 31% to 97% with the monomer variation range between 10% and 80%. In addition, the increased amount of crosslinker yielded higher DGs according to Figure 4.1(b).
- At the same radiation dose, a minor change in degree of grafting was obtained with an increase in the amount of DVB. The optimum amount of DVB has been taken as 3.5% since this amount yielded the desired level of DG at a low radiation dose.
- According to ATR-FTIR spectrum results of pristine ETFE, 61% PS grafted ETFE, and ETFE-*g*-PSSA, it is seen that the synthesis steps has been successfully followed.
- In the XPS surface analysis, it has been shown that meaningful changes in the atomic percentages of F and C elements took place. Also, when the surface changes of ETFE-*g*-PSSA membrane is examined, O atoms at approximately 532.2 eV and S atoms at 168.5 eV confirmed the presence of the sulfonic acid (-SO_3H) group.
- From the AFM images, it is seen that the surface roughness (Ra) increases because of grafting. On the other hand, Ra increases slightly from 53.9 to 60.4 after sulfonation of 61% grafted film. It indicates that both ETFE and PS do not undergo a severe morphological change during the sulfonation reaction.
- According to the DMA results, it was seen that the grafting of PS onto ETFE chains restricts the mobility of the backbone chains, causing an increase in the T_g value. Even a higher T_g (about 177 °C) for the ETFE-*g*-PSSA membrane with 87% DG confirms this interpretation.
- The experimental and theoretical IEC values appear to be entirely compatible with each other at a low degree of grafting. It seems that IEC increases with the degree of grafting. Therefore, the number of sulfonic acid groups in the membrane structure rises due to DG increase, as expected.
- ETFE-*g*-PSSA membranes with 45% and 67% degrees of grafting exhibited higher conductivity than many literature examples and commercially used Nafions, such as Nafion 112 membrane. However, the maximum proton conductivity attained in this thesis work at the higher degree of grafting (139.1 $mScm^{-1}$ at 67% DG) was lower compared to some previous literature data as the membranes were crosslinked in our case.

- A membrane synthesized in the absence of DVB exhibited significantly lower chemical stability compared to crosslinked ones. The non-crosslinked membrane degraded significantly after only about 100 hours, while samples prepared in the presence of DVB showed a similar level of degradation only beyond 400 hours. Despite the decrease in proton conductivity due to crosslinking through DVB use, there is a significant increase in the chemical stability of the membranes, indicating an important gain in favor of crosslinking.

REFERENCES

[1] G. Moad, E. Rizzardo, and S. H. Thang, “Radical addition-fragmentation chemistry in polymer synthesis,” *Polymer*, vol. 49, no. 5, pp. 1079–1131, 2008, doi: 10.1016/j.polymer.2007.11.020.

[2] M. Semsarilar and S. Perrier, “‘Green’ reversible addition-fragmentation chain-transfer (RAFT) polymerization,” *Nature Chemistry*, vol. 2, no. 10, pp. 811–820, 2010, doi: 10.1038/nchem.853.

[3] F. Barbir, *PEM Fuel Cells Theory and Practice*, 1st Editio. Academic Press, 2005.

[4] W. Mabrouk, “Synthesis and characterization of new protonic membranes. Proton exchange membrane fuel cell applications.” Dec. 2016.

[5] M. M. Nasef and E. S. A. Hegazy, “Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films,” *Progress in Polymer Science (Oxford)*, vol. 29, no. 6, pp. 499–561, 2004, doi: 10.1016/j.progpolymsci.2004.01.003.

[6] T. R. Dargaville, G. A. George, J. T. Hill, and A. K. Whittaker, “High energy radiation grafting of fluoropolymers,” *Prog. Polym. Sci.*, vol. 28, pp. 1355–1376, 2003.

[7] L. Gubler, S. A. Gürsel, and G. G. Scherer, “Radiation grafted membranes for polymer electrolyte fuel cells,” *Fuel Cells*, vol. 5, no. 3, pp. 317–335, 2005, doi: 10.1002/fuce.200400078.

[8] A. S. Aricò *et al.*, “Investigation of grafted ETFE-based polymer membranes as alternative electrolyte for direct methanol fuel cells,” *Journal of Power Sources*, vol. 123, no. 2, pp. 107–115, 2003, doi: 10.1016/S0378-7753(03)00528-7.

[9] G. Çelik, M. Barsbay, and O. Güven, “Towards new proton exchange membrane materials with enhanced performance via RAFT polymerization,” *Polymer Chemistry*, vol. 7, no. 3, pp. 701–714, 2016, doi: 10.1039/c5py01527h.

[10] L. Gubler, H. ben youcef, S. A. Gürsel, A. Wokaun, and G. G. Scherer, “Cross-Linker Effect in ETFE-Based Radiation-Grafted Proton-Conducting Membranes,” *Journal of The Electrochemical Society*, vol. 155, no. 9, p. B921, 2008, doi: 10.1149/1.2951919.

[11] T. Kallio *et al.*, “Electrochemical characterization of radiation-grafted ion-exchange membranes based on different matrix polymers.”

[12] L. Gubler, N. Prost, S. A. Gürsel, and G. G. Scherer, “Proton exchange membranes prepared by radiation grafting of styrene/divinylbenzene onto poly(ethylene-alt-tetrafluoroethylene) for low temperature fuel cells,” *Solid State Ionics*, vol. 176, no. 39–40, pp. 2849–2860, 2005, doi: 10.1016/j.ssi.2005.09.045.

[13] H. ben youcef, S. A. Gürsel, A. Wokaun, and G. G. Scherer, “The influence of crosslinker on the properties of radiation-grafted films and membranes based on ETFE,” *Journal of Membrane Science*, vol. 311, no. 1–2, pp. 208–215, Mar. 2008, doi: 10.1016/j.memsci.2007.12.015.

[14] H. Ren and J. Chae, “Fuel cells technologies for wireless MEMS,” *Wireless MEMS Networks and Applications*, vol. 2, pp. 35–51, 2017, doi: 10.1016/B978-0-08-100449-4.00002-6.

[15] S. Curtin and J. Gangi, “The Business Case for Fuel Cells 2013: Reliability, Resiliency & Savings,” *Fuel Cells 2000 - Breakthrough Technologies Institute*, 2013.

[16] W. R. Grove, “XXIV. On voltaic series and the combination of gases by platinum,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 14, no. 86–87, pp. 127–130, Feb. 1839, doi: 10.1080/14786443908649684.

[17] M. Will, *Fuel Cells*. San Diego: Academic Press Incorporated, 1963.

[18] U. Bossel, *The Birth of Fuel Cell 1835-1845*. European Fuel Cell Forum, 2000.

[19] W. R. Grove, “LXXII. On a gaseous voltaic battery,” *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, vol. 21, no. 140, pp. 417–420, Dec. 1842, doi: 10.1080/14786444208621600.

[20] G. Hoogers, *Fuel Cell Technology Handbook*, First edit. CRC Press, 2003.

[21] K. D. Kreuer, “On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells,” *Journal of Membrane Science*, vol. 185, no. 1, pp. 29–39, 2001, doi: 10.1016/S0376-7388(00)00632-3.

[22] M. Nadal and F. Barbir, “Development of a hybrid fuel cell/battery powered electric vehicle,” *International Journal of Hydrogen Energy*, vol. 21, no. 6, pp. 497–505, 1996, doi: 10.1016/0360-3199(95)00102-6.

[23] C. Stone and A. E. Morrison, “From curiosity to ‘power to change the world®,’” *Solid State Ionics*, vol. 152–153, pp. 1–13, 2002, doi: 10.1016/S0167-2738(02)00315-6.

[24] L. James and A. Dicks, *Fuel Cell Systems Explained*. UK: John Wiley and Sons, 2000.

[25] K. Adamson, “Hydrogen from renewable resources - the hundred year commitment,” *Energy Policy*, vol. 32, no. 10, pp. 1231–1242, 2004.

[26] A. C. Fărcaş and P. Dobra, “Adaptive Control of Membrane Conductivity of PEM Fuel Cell,” *Procedia Technology*, vol. 12, pp. 42–49, 2014, doi: 10.1016/j.protcy.2013.12.454.

[27] Ö. Başkan, S. Haldenbilen, and H. Ceylan, “Ulaştırma sektörünün enerji talebinin modellenmesi ve sürdürülebilir politikalar,” 2006.

[28] R. P. O’Hayre, S.-W. Cha, W. G. Colella, and F. B. Prinz, *Fuel Cell Fundamentals*. USA: John Wiley & Sons, 2009.

[29] H. ben youcef, L. Gubler, S. A. Gürsel, D. Henkensmeier, A. Wokaun, and G. G. Scherer, “Novel ETFE based radiation grafted poly(styrene sulfonic acid-co-methacrylonitrile) proton conducting membranes with increased stability,” *Electrochemistry Communications*, vol. 11, no. 5, pp. 941–944, 2009, doi: 10.1016/j.elecom.2009.02.047.

[30] X. Li and I. Sabir, “Review of bipolar plates in PEM fuel cells: Flow-field designs,” *International Journal of Hydrogen Energy*, vol. 30, no. 4, pp. 359–371, 2005, doi: 10.1016/j.ijhydene.2004.09.019.

[31] K. D. Kreuer, A. Rabenau, and W. Weppner, “A Stable Tetraalkoxy(hydroxy)phosphorane and Phosphorane Oxide Anion by Hydrolysis of Tetraalkoxy(halogen)phosphoranes,” *Angew. Chem. Int. Ed.*, vol. 21, p. 208, 1982.

[32] G. G. Scherer, “Polymer Membranes for Fuel Cells,” *Berichte der Bunsengesellschaft für physikalische Chemie*, vol. 94, pp. 1008–1004, 1990.

[33] Q. Li, R. He, J. O. Jensen, and N. J. Bjerrum, “Approaches and Recent Development of Polymer Electrolyte Membranes for Fuel Cells Operating above 100 °C,” *Chemistry of Materials*, vol. 15, no. 26, pp. 4896–4915, 2003, doi: 10.1021/cm0310519.

[34] P. R. Resnick and G. W. Grot, “E.I. du Pont de Nemours and Company,” 4113585, 1978

[35] K. A. Mauritz and R. B. Moore, “State of understanding of Nafion,” *Chemical Reviews*, vol. 104, no. 10, pp. 4535–4585, 2004, doi: 10.1021/cr0207123.

[36] F. Barbir and T. Gómez, “Efficiency and economics of proton exchange membrane (PEM) fuels cells,” *International Journal of Hydrogen Energy*, vol. 21, no. 10, pp. 891–901, 1996, doi: 10.1016/0360-3199(96)00030-4.

[37] B. Yang, “Development of New Membranes for Proton Exchange Membrane and Direct Methanol Fuel Cells,” The University of Texas at Austin, 2004.

[38] S. J. Peighambardoust, S. Rowshanzamir, and M. Amjadi, *Review of the proton exchange membranes for fuel cell applications*, vol. 35, no. 17. Elsevier Ltd, 2010. doi: 10.1016/j.ijhydene.2010.05.017.

[39] B. Smitha, S. Sridhar, and A. A. Khan, “Solid polymer electrolyte membranes for fuel cell applications - A review,” *Journal of Membrane Science*, vol. 259, no. 1–2, pp. 10–26, 2005, doi: 10.1016/j.memsci.2005.01.035.

[40] D. J. Jones and J. Roziere, “Recent advances in the functionalisation of polybenzimidazole and polyetherketone for fuel cell applications,” *J. Membr. Sci.*, vol. 185, pp. 41–58, 2001.

[41] A. Bhattacharya and B. N. Misra, “Grafting: A versatile means to modify polymers: Techniques, factors and applications,” *Progress in Polymer Science (Oxford)*, vol. 29, no. 8, pp. 767–814, 2004, doi: 10.1016/j.progpolymsci.2004.05.002.

[42] J. Mosa, A. Durán, and M. Aparicio, “Proton conducting sol-gel sulfonated membranes produced from 2-allylphenol, 3-glycidoxypropyl trimethoxysilane and tetraethyl orthosilicate,” *Journal of Power Sources*, vol. 192, no. 1, pp. 138–143, 2009, doi: 10.1016/j.jpowsour.2008.12.126.

[43] E. Y. Choi, H. Strathmann, J. M. Park, and S. H. Moon, “Characterization of non-uniformly charged ion-exchange membranes prepared by plasma-induced graft polymerization,” *Journal of Membrane Science*, vol. 268, no. 2, pp. 165–174, 2006, doi: 10.1016/j.memsci.2005.06.052.

[44] J. Chen, M. Asano, T. Yamaki, and M. Yoshida, “Preparation and characterization of chemically stable polymer electrolyte membranes by radiation-induced graft copolymerization of four monomers into ETFE films,” *Journal of Membrane Science*, vol. 269, no. 1–2, pp. 194–204, 2006, doi: 10.1016/j.memsci.2005.06.035.

[45] F. N. Büchi, B. Gupta, O. Haas, and G. G. Scherer, “Study of radiation-grafted FEP-G-polystyrene membranes as polymer electrolytes in fuel cells,”

Electrochimica Acta, vol. 40, no. 3, pp. 345–353, 1995, doi: 10.1016/0013-4686(94)00274-5.

[46] S. Alkan Gürsel, L. Gubler, B. Gupta, and G. G. Scherer, “Radiation grafted membranes,” *Advances in Polymer Science*, vol. 215, no. 1, pp. 157–217, 2008, doi: 10.1007/12_2008_153.

[47] S. Alkan Gürsel, L. Gubler, B. Gupta, and G. G. Scherer, “Radiation grafted membranes,” *Advances in Polymer Science*, vol. 215, no. 1, pp. 157–217, 2008, doi: 10.1007/12_2008_153.

[48] M. M. Nasef, H. Saidi, and H. M. Nor, “Radiation induced graft copolymerization for preparation of cation exchange membranes: a review,” *Jurnal Sains Nuklear Malaysia*, vol. 17, no. 1, pp. 27–43, 1999.

[49] B. Gupta and G. Scherer, “Proton exchange membranes by radiation-induced graft copolymerization of monomers into Teflon-FEP films,” *Chimia*, vol. 48, pp. 127–137, 1999.

[50] S. A. Gürsel, H. Yousef, A. Wokaun, and G. G. Scherer, “Influence of reaction parameters on grafting of styrene into poly(ethylene-alt- tetrafluoroethylene) films,” *Nuc. Inst. and Methods in Physics Reaserch B*, vol. 265, pp. 198–203, 2007.

[51] R. Rohani, M. M. Nasef, H. Saidi, and K. Z. M. Dahlan, “Effect of reaction conditions on electron induced graft copolymerization of styrene onto poly(ethylene-co-tetrafluoroethylene) films: kinetic study,” *Chem. Eng. J.*, vol. 132, pp. 27–35, 2007.

[52] Y. Kimura, M. Asano, J. Chen, Y. Maekawa, R. Katakai, and M. Yoshida, “Influence of grafting solvents on the properties of polymer electrolyte membranes prepared by γ-ray preirradiation method,” *Radiation Physics and Chemistry*, vol. 77, no. 7, pp. 864–870, 2008, doi: 10.1016/j.radphyschem.2007.12.012.

[53] U. Septiani, J. Chen, M. Asano, Y. Maekawa, M. Yoshida, and H. Kubota, “Influence of pre-irradiation condition on the properties of polymer electrolyte membranes prepared using radiation grafting,” *J. Mater. Sci.*, vol. 42, pp. 1330–1335, 2007.

[54] E. Chen, M. Asano, T. Yamaki, and M. Yoshida, “Preparation of sulfonated crosslinked PTFE-graft-poly(alkyl vinyl ether) membranes for polymer electrolyte membrane fuel cells by radiation processing,” *J. Membr. Sci.*, vol. 256, pp. 38–45, 2005.

[55] G. Çelik, “Poli(etilen-alt-tetrafloroetilen) (ETFE) Ardışık Kopolimer Filmine Raft Yöntemi ve Radyasyon Kullanılarak Stiren Aşılanması ve Yakıt Pili Membranı Hazırlanması,” 2013.

[56] M. Barsbay, O. Güven, M. H. Stenzel, T. P. Davis, C. Barner-Kowollik, and L. Barner, “Verification of controlled grafting of styrene from cellulose via radiation-induced RAFT polymerization,” *Macromolecules*, vol. 40, no. 20, pp. 7140–7147, 2007, doi: 10.1021/ma070825u.

[57] M. Barsbay and O. Güven, “RAFT mediated grafting of poly(acrylic acid) (PAA) from polyethylene/polypropylene (PE/PP) nonwoven fabric via preirradiation,” *Polymer*, vol. 54, no. 18, pp. 4838–4848, 2013.

[58] Y. Kodama, M. Barsbay, and O. Güven, “Poly(2-hydroxyethyl methacrylate) (PHEMA) grafted polyethylene/polypropylene (PE/PP) nonwoven fabric by gamma-initiation: Synthesis, characterization and benefits of RAFT mediation,” *Radiat. Physic. Chem.*, vol. 105, pp. 31–38, 2014.

[59] K. Matyjaszewski and J. Spanswick, “Controlled/living radical polymerization,” *Materials Today*, vol. 8, no. 3, pp. 26–33, 2005, doi: 10.1016/S1369-7021(05)00745-5.

[60] K. Matyjaszewski and W. A. Braunecker, “Radical Polymerization,” *Macromolecular Engineering*. pp. 161–215, Sep. 23, 2011. doi: https://doi.org/10.1002/9783527631421.ch5.

[61] O. W. Webster, “Living polymerization methods,” *Science*, vol. 4996, no. 251, pp. 887–893, 1991, doi: 10.1126/science.251.4996.887.

[62] H. Arslan, “Block and Graft Copolymerization by Controlled/Living Radical Polymerization Methods,” in *Polymerization*, A. D. S. Gomes, Ed. Rijeka: IntechOpen, 2012. doi: 10.5772/45970.

[63] D. Konkolewicz, B. Hawkett, A. Gray-Weale, and S. Perrier, “RAFT Polymerization Kinetics: Combination of Apparently Conflicting Models,” *Macromolecules*, vol. 41, pp. 6400–6412, Sep. 2008, doi: 10.1021/ma800388c.

[64] J.-S. Wang and K. Matyjaszewski, “Controlled/"living" radical polymerization. atom transfer radical polymerization in the presence of transition-metal complexes,” *Journal of the American Chemical Society*, vol. 117, no. 20, pp. 5614–5615, May 1995, doi: 10.1021/ja00125a035.

[65] G. Kickelbick, H. Paik, and K. Matyjaszewski, “Immobilization of the Copper Catalyst in Atom Transfer Radical Polymerization,” *Macromolecules*, vol. 32, no. 9, pp. 2941–2947, May 1999, doi: 10.1021/ma9818432.

[66] K. MATYJASZEWSKI and S. G. GAYNOR, “FREE RADICAL POLYMERIZATION,” in *Applied Polymer Science: 21st Century*, C. D. Craver and C. E. Carraher, Eds. Oxford: Pergamon, 2000, pp. 929–977. doi: https://doi.org/10.1016/B978-008043417-9/50046-5.

[67] P. Trapa, B. Huang, Y.-Y. Won, D. Sadoway, and A. Mayes, “Block Copolymer Electrolytes Synthesized by Atom Transfer Radical Polymerization for Solid-State, Thin-Film Lithium Batteries,” *Electrochemical and Solid State Letters - ELECTROCHEM SOLID STATE LETT*, vol. 5, May 2002, doi: 10.1149/1.1461996.

[68] M. Kato, M. Kamigaito, M. Sawamoto, and T. Higashimura, “Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris-(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization,” *Macromolecules*, vol. 28, no. 5, pp. 1721–1723, Feb. 1995, doi: 10.1021/ma00109a056.

[69] K. Matyjaszewski, K. Davis, T. E. Patten, and M. Wei, “Observation and analysis of a slow termination process in the atom transfer radical polymerization of styrene,” *Tetrahedron*, vol. 53, no. 45, pp. 15321–15329, 1997, doi: https://doi.org/10.1016/S0040-4020(97)00965-4.

[70] K. Matyjaszewski and J. Xia, “Atom Transfer Radical Polymerization,” *Chemical Reviews*, vol. 101, no. 9, pp. 2921–2990, Sep. 2001, doi: 10.1021/cr940534g.

[71] M. Kamigaito, T. Ando, and M. Sawamoto, “Metal-Catalyzed Living Radical Polymerization,” *Chemical Reviews*, vol. 101, no. 12, pp. 3689–3746, Dec. 2001, doi: 10.1021/cr9901182.

[72] C. J. Hawker, A. W. Bosman, and E. Harth, “New polymer synthesis by nitroxide mediated living radical polymerizations,” *Chemical Reviews*, vol. 101, no. 12, pp. 3661–3688, 2001, doi: 10.1021/cr990119u.

[73] D. Konkolewicz, O. Thorn-Seshold, and A. Gray-Weale, “Models for randomly hyperbranched polymers: Theory and simulation.,” *The Journal of chemical physics*, vol. 129, no. 5, p. 54901, Aug. 2008, doi: 10.1063/1.2939242.

[74] C. J. Hawker, G. G. Barclay, and J. Dao, “Radical Crossover in Nitroxide Mediated ‘Living’ Free Radical Polymerizations,” *Journal of the American Chemical Society*, vol. 118, no. 46, pp. 11467–11471, Jan. 1996, doi: 10.1021/ja9624228.

[75] S. Perrier, “50th Anniversary Perspective: RAFT Polymerization - A User Guide,” *Macromolecules*, vol. 50, no. 19, pp. 7433–7447, 2017, doi: 10.1021/acs.macromol.7b00767.

[76] D. J. Keddie, “A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization,” *Chemical Society Reviews*, vol. 43, no. 2, pp. 496–505, 2014, doi: 10.1039/c3cs60290g.

[77] S. W. Prescott, M. J. Ballard, E. Rizzardo, and R. G. Gilbert, “Successful Use of RAFT Techniques in Seeded Emulsion Polymerization of Styrene: Living Character, RAFT Agent Transport, and Rate of Polymerization,” *Macromolecules*, vol. 35, no. 14, pp. 5417–5425, Jul. 2002, doi: 10.1021/ma011840g.

[78] G. Moad, E. Rizzardo, and S. H. Thang, “Living Radical Polymerization by the RAFT Process A Second Update,” *Australian Journal of Chemistry*, vol. 62, no. 11, pp. 1402–1472, 2009.

[79] C. Grande, M. Tria, G. Jiang, R. Ponnapati, F. Zuluaga, and R. Advincula, “Grafting of polymers from electrodeposited macro-RAFT initiators on conducting surfaces,” *Reactive & Functional Polymers - REACT FUNCT POLYM*, vol. 71, pp. 938–942, Sep. 2011, doi: 10.1016/j.reactfunctpolym.2011.05.013.

[80] M. G. Fröhlich, M. M. Nardai, N. Förster, P. Vana, and G. Zifferer, “Shielding effects in polymer–polymer reactions, 3. Z-RAFT star polymerization under various solvent conditions,” *Polymer*, vol. 51, no. 22, pp. 5122–5134, 2010, doi: https://doi.org/10.1016/j.polymer.2010.08.054.

[81] T. Duong, C. Bressy, and A. Margaillan, “Well-defined diblock copolymers of poly(tert-butyldimethylsilyl methacrylate) and poly(dimethylsiloxane) synthesized by RAFT polymerization,” *Polymer*, vol. 55, pp. 39–47, Jan. 2014, doi: 10.1016/j.polymer.2013.11.034.

[82] E. Rizzardo, M. Chen, B. Chong, G. Moad, M. Skidmore, and S. H. Thang, “RAFT polymerization: Adding to the picture,” *Macromolecular Symposia*, vol. 248, pp. 104–116, 2007, doi: 10.1002/masy.200750211.

[83] Y. A. Vasilieva *et al.*, “Controlled/living polymerization of methacrylamide in aqueous media via the RAFT process,” *Journal of Polymer Science, Part A:*

Polymer Chemistry, vol. 43, no. 14, pp. 3141–3152, 2005, doi: 10.1002/pola.20786.

[84] B. Y. K. Chong *et al.*, “Thiocarbonylthio compounds [S=C(Ph)S-R) in free radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization). Role of the free-radical leaving group (R),” *Macromolecules*, vol. 36, no. 7, pp. 2256–2272, 2003, doi: 10.1021/ma020882h.

[85] G. Moad *et al.*, “Living free radical polymerization with reversible addition-fragmentation chain transfer (the life of RAFT),” *Polymer International*, vol. 49, no. 9, pp. 993–1001, 2000, doi: 10.1002/1097-0126(200009)49:9<993::AID-PI506>3.0.CO;2-6.

[86] C. Barner-kowollik, *Polyolefin Reaction Engineering Macromolecular Engineering Principles of Polymerization Principles of Polymer Processing 2e Colloids and Interfaces with Surfactants and Polymers - An Introduction Introduction to Polymer Viscoelasticity Handbook of Polymer*. 2007.

[87] H. Willcock and R. K. O’Reilly, “End group removal and modification of RAFT polymers,” *Polymer Chemistry*, vol. 1, no. 2, pp. 149–157, 2010, doi: 10.1039/b9py00340a.

[88] C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Liu, and S. Perrier, “Bioapplications of RAFT polymerization,” *Chemical Reviews*, vol. 109, no. 11, pp. 5402–5436, 2009, doi: 10.1021/cr9001403.

[89] M. Beija, J. D. Marty, and M. Destarac, “RAFT/MADIX polymers for the preparation of polymer/inorganic nanohybrids,” *Progress in Polymer Science (Oxford)*, vol. 36, no. 7, pp. 845–886, 2011, doi: 10.1016/j.progpolymsci.2011.01.002.

[90] C. K. Kuşçuoğlu, H. Güner, M. A. Söylemez, O. Güven, and M. Barsbay, “A smartphone-based colorimetric PET sensor platform with molecular recognition via thermally initiated RAFT-mediated graft copolymerization,” *Sensors and Actuators, B: Chemical*, vol. 296, no. June, 2019, doi: 10.1016/j.snb.2019.126653.

[91] L. Li, T. Nakaji-Hirabayashi, H. Kitano, K. Ohno, Y. Saruwatari, and K. Matsuoka, “A novel approach for UV-patterning with binary polymer brushes,” *Colloids and Surfaces B: Biointerfaces*, vol. 161, pp. 42–50, 2018, doi: https://doi.org/10.1016/j.colsurfb.2017.10.022.

[92] M. Barsbay, Y. Kodama, and O. Güven, "Functionalization of cellulose with epoxy groups via γ-initiated RAFT-mediated grafting of glycidyl methacrylate," *Cellulose*, vol. 21, no. 6, pp. 4067–4079, 2014, doi: 10.1007/s10570-014-0416-y.

[93] Z. Liu, G. Zhang, W. Lu, Y. Huang, J. Zhang, and T. Chen, "UV light-initiated RAFT polymerization induced self-assembly," *Polymer Chemistry*, vol. 6, no. 34, pp. 6129–6132, 2015, doi: 10.1039/c5py00907c.

[94] M. Barsbay and O. Güven, "A short review of radiation-induced raft-mediated graft copolymerization: A powerful combination for modifying the surface properties of polymers in a controlled manner," *Radiation Physics and Chemistry*, vol. 78, no. 12, pp. 1054–1059, 2009, doi: 10.1016/j.radphyschem.2009.06.022.

[95] S. Holmberg *et al.*, "Versatile synthetic route to tailor-made proton exchange membranes for fuel cell applications by combination of radiation chemistry of polymers with nitroxide-mediated living free radical graft polymerization," *Macromolecules*, vol. 37, no. 26, pp. 9909–9915, 2004, doi: 10.1021/ma0353641.

[96] Z. Maolin, J. Chen, S. Hasegawa, and Y. Maekawa, "Synthesis of fluorinated polymer electrolyte membranes by radiation grafting and atom transfer radical polymerization techniques," *Polymer*, vol. 50, pp. 1159–1165, Feb. 2009, doi: 10.1016/j.polymer.2009.01.014.

[97] K. SH and C. CG, "Synthesis and Characterization of Well Defined Polysulfone-g-Poly(styrenesulfonic acid) Graft Copolymers for Proton Exchange Membrane," *Macromolecular Research*, vol. 19, no. 11, pp. 1142–1150, 2011, doi: 10.1007/s13233-011-1101-8.

[98] G. Çelik, M. Barsbay, and O. Güven, "Towards new proton exchange membrane materials with enhanced performance via RAFT polymerization," *Polymer Chemistry*, vol. 7, no. 3, 2016, doi: 10.1039/c5py01527h.

[99] Q. Yu, M. Zhou, Y. Ding, B. Jiang, and S. Zhu, "Development of networks in atom transfer radical polymerization of dimethacrylates," *Polymer*, vol. 48, pp. 7058–7064, Nov. 2007, doi: 10.1016/j.polymer.2007.10.001.

[100] C. Jiang, Y. Shen, S. Zhu, and D. Hunkeler, "Gel formation in atom transfer radical polymerization of 2-(N,N-dimethylamino)ethyl methacrylate and ethylene glycol dimethacrylate," *Journal of Polymer Science, Part A: Polymer Chemistry*, vol. 39, no. 21, pp. 3780–3788, 2001, doi: 10.1002/pola.10023.

[101] T. Tanaka, T. Suzuki, Y. Saka, P. Zetterlund, and M. Okubo, "Mechanical properties of cross-linked polymer particles prepared by nitroxide-mediated

radical polymerization in aqueous micro-suspension," *Polymer*, vol. 48, pp. 3836–3843, Jun. 2007, doi: 10.1016/j.polymer.2007.04.040.

[102] N. Ide and T. Fukuda, "Nitroxide-controlled free-radical copolymerization of vinyl and divinyl monomers. 2. Gelation," *Macromolecules*, vol. 32, no. 1, pp. 95–99, 1999, doi: 10.1021/ma9805349.

[103] M. M. Titirici and B. Sellergren, "Thin molecularly imprinted polymer films via reversible addition-fragmentation chain transfer polymerization," *Chemistry of Materials*, vol. 18, no. 7, pp. 1773–1779, 2006, doi: 10.1021/cm052153x.

[104] R. Henkel and P. Vana, "The influence of RAFT on the microstructure and the mechanical properties of photopolymerized poly(butyl acrylate) networks," *Macromolecular Chemistry and Physics*, vol. 215, no. 2, pp. 182–189, 2014, doi: 10.1002/macp.201300581.

[105] Q. Yu, Y. Zhu, Y. Ding, and S. Zhu, "Reaction behavior and network development in RAFT radical polymerization of dimethacrylates," *Macromolecular Chemistry and Physics*, vol. 209, no. 5, pp. 551–556, 2008, doi: 10.1002/macp.200700464.

[106] M. A. D. Gonçalves, V. D. Pinto, R. C. S. Dias, J. C. Hernándes-Ortiz, and M. R. P. F. N. Costa, "Dynamics of network formation in aqueous suspension RAFT styrene/divinylbenzene copolymerization," *Macromolecular Symposia*, vol. 333, no. 1, pp. 273–285, 2013, doi: 10.1002/masy.201300046.

[107] M. Akbulut, M. Barsbay, and O. Güven, "Radyasyona bağlı RAFT polimerizasyonu yoluyla moleküler baskılanmış polimer sisteminin hazırlanması için bir yöntem," FPT-2015-6837, 2015

[108] X. Tian, J. Ding, B. Zhang, F. Qiu, X. Zhuang, and Y. Chen, "Recent advances in RAFT polymerization: Novel initiation mechanisms and optoelectronic applications," *Polymers*, vol. 10, no. 3, 2018, doi: 10.3390/polym10030318.

[109] N. Pullan, M. Liu, and P. D. Topham, "Reversible addition-fragmentation chain transfer polymerization of 2-chloro-1,3-butadiene," *Polymer Chemistry*, vol. 4, no. 7, pp. 2272–2277, 2013, doi: 10.1039/c3py21151g.

[110] H. P. Brack, H. G. Buhrer, L. Bonorand, and G. G. Scherer, "Grafting of pre-irradiated poly(ethylene-alt-tetrafluoroethylene) films with styrene: Influence of base polymer film properties and processing parameters," *Journal of Materials Chemistry*, vol. 10, no. 8, pp. 1795–1803, 2000, doi: 10.1039/b001851l.

[111] G. G. Scherer, “Interfacial aspects in the development of polymer electrolyte fuel cells,” *Solid State Ionics*, vol. 94, no. 1–4. Elsevier, pp. 249–257, Feb. 01, 1997. doi: 10.1016/s0167-2738(96)00616-9.

[112] A. Chapiro, *Radiation Chemisrty of Polymeric Systems*. New York: Wiley-Interscience, 1962.

[113] F. Wallasch, “Investigation on radiation grafted polymer fuel cell membranes: preparation, characterization, applications,” Swiss Federal Instutie of Technology, Zurih, 2010.

[114] T. Ovalıoğlu, “Stirenin Çapraz Bağlayıcı ve Raft Ajanı Varlığında İyonlaştırıcı Radyasyonla Polimerizasyonu,” Hacettepe Üniversitesi, 2015.

[115] S. Radice, N. Del Fanti, C. Castiglioni, M. Del Zoppo, and G. Zerbi, “Vibrational Analysis as a Tool for Detecting Electronic Mobility. The Case of the Alternating Ethylene-Tetrafluoroethylene Copolymers,” *Macromolecules*, vol. 27, no. 8, pp. 2194–2199, 1994, doi: 10.1021/ma00086a032.

[116] X. Xu, R. W. M. Kwok, and W. M. Lau, “Surface modification of polystyrene by low energy hydrogen ion beam,” *Thin Solid Films*, vol. 514, no. 1–2, pp. 182–187, 2006, doi: 10.1016/j.tsf.2006.02.095.

[117] M. M. Nasef and H. Saidi, “Surface studies of radiation grafted sulfonic acid membranes: XPS and SEM analysis,” *Applied Surface Science*, vol. 252, no. 8, pp. 3073–3084, 2006, doi: 10.1016/j.apsusc.2005.05.013.

[118] H. Brack, M. Wyler, G. Peter, and G. Scherer, “A contact angle investigation of the surface properties of selected proton-conducting radiation-grafted membranes,” *Journal of Membrane Science - J MEMBRANE SCI*, vol. 214, pp. 1–19, Mar. 2003, doi: 10.1016/S0376-7388(02)00390-3.

[119] S. A. Gürsel, J. Schneider, H. ben Youcef, A. Wokaun, and G. G. Scherer, “Thermal properties of proton-conducting radiation-grafted membranes,” *Journal of Applied Polymer Science*, vol. 108, no. 6, pp. 3577–3585, Jun. 2008, doi: 10.1002/app.27947.

[120] R. Y. M. Huang, P. Shao, C. M. Burns, and X. Feng, “Sulfonation of poly(ether ether ketone)(PEEK): Kinetic study and characterization,” *J. Appl. Polym. Sci.*, vol. 82, p. 2651, 2001.

[121] L. P. Blanchard, V. Hornof, H. H. Lam, and S. L. Malhotra, “Thermal decomposition of polystyrene, polyoxyethylene glycol and their mixtures by

thermogravimetric techniques," *European Polymer Journal*, vol. 10, no. 11, pp. 1057–1067, Nov. 1974, doi: 10.1016/0014-3057(74)90071-8.

[122] L. Li *et al.*, "A novel approach to prepare proton exchange membranes from fluoropolymer powder by pre-irradiation induced graft polymerization," *Journal of Membrane Science*, vol. 346, no. 1, pp. 113–120, 2010, doi: 10.1016/j.memsci.2009.09.027.

[123] T. A. Zawodzinski, T. E. Springer, F. Uribe, and S. Gottesfeld, "Characterization of polymer electrolytes for fuel cell applications," *Solid State Ionics*, vol. 60, no. 1–3, pp. 199–211, Mar. 1993, doi: 10.1016/0167-2738(93)90295-E.

[124] R. Borup *et al.*, "Scientific aspects of polymer electrolyte fuel cell durability and degradation," *Chemical Reviews*, vol. 107, no. 10, pp. 3904–3951, 2007, doi: 10.1021/cr050182l.

[125] G. Hubner and E. Roduner, "EPR investigation of HO radical initiated degradation reactions of," *Journal of Materials Chemistry*, pp. 409–418, 1999.

[126] S. Stucki, S. GG, S. Schlagowski, and E. Fischer, "PEM water electrolysers: evidence for membrane failure in 100 kW demonstration plants," *Journal of Applied Electrochemistry*, vol. 28, no. 10, pp. 1041–1049, 1998, doi: 10.1023/A:1003477305336.

[127] J. Yu *et al.*, "Degradation mechanism of polystyrene sulfonic acid membrane and application of its composite membranes in fuel cells," *Physical Chemistry Chemical Physics*, vol. 5, no. 3, pp. 611–615, 2003, doi: 10.1039/b209020a.

[128] M. M. Nasef, H. Saidi, and A. H. Yahaya, "Radiation-induced Grafting of Styrene onto Polyethylene Films for Preparation of Cation Exchange Membranes: Effect of Crosslinking+," *Journal of Applied Membrane Science & Technology*, vol. 2, no. 1, Nov. 2017, doi: 10.11113/amst.v2i1.4.